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EFFICIENT FREE-ENERGY CALCULATIONS BY THE SIMULATION OF NONEQUILIBRIUM PROCESSES

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ALONG WITH THE IMPRESSIVE PROGRESS OF COMPUTER TECHNOLOGY OVER THE PAST THREE DECADES, COMPUTATIONAL PHYSICS HAS EVOLVED INTO A DYNAMIC DISCIPLINE THAT

plays an important role in many different fields. Its contribution has been particularly profound in the areas of condensed-matter physics, chemistry, and materials science, where most problems involve complex many-body systems. In the overwhelming majority of cases it is impossible to obtain analytical solutions to these problems, and numerical techniques are generally the only realistic option.

In this column we discuss a particular application of computational physics: the calculation of thermodynamic properties by computer simulation methods. More specifically, we focus on one of the most difficult tasks in this context: the estimation of free energies in problems such as the study of phase transformations in solids and liquids, the influence of lattice defects on the mechanical properties of technological materials, the kinetics of chemical reactions, and protein-folding mechanisms in biological processes. Because the free energy plays a fundamental role, the development of efficient and accurate techniques for its calculation has attracted considerable attention during the past 15 years and is still an active field of research. Here we will discuss some general aspects of equilibrium and nonequilibrium approaches to free-energy measurement, and present the *reversible-scaling* technique, which we have recently developed.¹

Free-energy calculations by computer simulations

The calculation of thermodynamic properties is rooted in the framework of equilibrium statistical mechanics, which expresses many thermodynamic properties (for example, the internal energy and the enthalpy) in terms of statistical averages over particular probability distribution functions. Computer simulation techniques provide powerful algorithms for the sampling of these distribution functions, and

standard simulation techniques such as Metropolis Monte Carlo and molecular dynamics allow the straightforward evaluation of the thermodynamic averages.²⁻⁵

The calculation of free energies, however, is more complicated. The reason is that the free energy cannot be written directly in terms of statistical averages. Instead, it depends explicitly on the partition function, which is the normalization factor of the statistical mechanical-distribution functions. Consequently, the standard sampling methods used to determine thermodynamic averages do not provide direct information for free energies.

To clarify the nature of this problem, we consider an example due to Daan Frenkel.⁶ Suppose we measure the average depth of a lake in a way equivalent to the approach adopted in a typical computer simulation. In a small boat we “sample” the lake surface, performing a series of depth measurements at random positions on the lake. Although this information could give an accurate estimate of the average lake depth after many measurements, we would not have a reliable estimate for the area A of the lake surface.

In this simple example we have sampled from a distribution function describing the probability of finding the boat on a certain surface element of the lake. The sampling procedure provides direct information on the *relative* probabilities—that is, the probability of finding the boat on surface element a relative to the probability of finding it on element b . This information is sufficient for the calculation of the average depth, but the procedure does not provide direct information on the absolute probability distribution function $1/A$, where the area A represents the absolute normalization factor.

The problem sketched in this example is identical to the situation we encounter in the standard computer simulation algorithms used to evaluate thermodynamic averages. The Metropolis sampling algorithm guarantees a correct sampling from a distribution that is only proportional to the absolute probability distribution function. Although this algorithm provides a correct description of the relative probabilities of system configurations and suffices for the calculation of ensemble averages, it does not lead to direct determination of the partition function and consequently

the free energy. For this reason, the computation of free energies by computer simulation methods can be accomplished only by using indirect strategies and is generally computationally expensive.

Equilibrium estimations of free-energy differences

The *thermodynamic integration* method is the prototypical example of such an indirect approach. It exploits the fact that several of the derivatives of the free energy can be expressed in terms of equilibrium ensemble averages. The thermodynamic-integration method constructs free-energy differences by the numerical integration of such a derivative using the averages determined from sequences of independent equilibrium simulations.

One of the most powerful and flexible applications of this approach involves the calculation of free-energy differences between two systems characterized by different Hamiltonians. This application relies on the evaluation of the work done along a quasistatic process⁷ in which the Hamiltonian of one system is transformed into that of the other.² This process, defined as a continuous sequence of equilibrium states, is described by a coupled Hamiltonian $H(\lambda)$ that, aside from the usual dependence on particle positions and momenta, is also a function of some generalized coordinate λ . Usually, $H(\lambda)$ is constructed in such a way that it features a transformation from the Hamiltonian of a system of interest H_{sys} to that of some reference system H_{ref} for which the free energy is known beforehand. An example of such a transformation is the simple linear interpolation

$$H(\lambda) = (1 - \lambda)H_{\text{sys}} + \lambda H_{\text{ref}} \quad (1)$$

where the coupled system $H(\lambda)$ transforms continuously from the system of interest H_{sys} to the reference system H_{ref} as λ changes from 0 to 1.

Using this construction, the idea is to evaluate the free-energy difference between the system of interest and the reference system. From the exact expression for the free energy $F(\lambda)$ of the coupled system $H(\lambda)$, it follows that the free-energy difference can be written as the work W_{qs} done along a quasistatic process.² To obtain this relation, we give this expression explicitly:

$$\begin{aligned} F(\lambda) &= -k_B T \ln Z(\lambda) \\ &= -k_B T \ln \left[\int d\Gamma \exp[-H(\lambda)/k_B T] \right] \end{aligned} \quad (2)$$

where $Z(\lambda)$ is the partition function, k_B is Boltzmann's constant, and T is the temperature. The integration is carried

out over all phase space Γ . The derivative of $F(\lambda)$ with respect to λ is then given by

$$\begin{aligned} \frac{\partial F(\lambda)}{\partial \lambda} &= \frac{\int d\Gamma (\partial H(\lambda)/\partial \lambda) \exp[-H(\lambda)/k_B T]}{Z(\lambda)} \\ &= \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle_{\lambda} \end{aligned} \quad (3)$$

where $\partial H(\lambda)/\partial \lambda$ represents the driving force for the quasistatic process and the brackets $\langle \dots \rangle_{\lambda}$ denote an ensemble average for the system described by $H(\lambda)$.

Accordingly, the free-energy difference between the system of interest and the reference system may be written as

$$\begin{aligned} F(\lambda_2) - F(\lambda_1) &= \int_{\lambda_1}^{\lambda_2} d\lambda \frac{\partial F(\lambda)}{\partial \lambda} \\ &= \int_{\lambda_1}^{\lambda_2} d\lambda \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle_{\lambda} \equiv W_{\text{qs}} \end{aligned} \quad (4)$$

where λ_1 and λ_2 represent the systems of interest and reference system, respectively. Hence, we see that the free-energy difference between the two systems is equal to the total work W_{qs} along the quasistatic process, defined as the integration of the equilibrium ensemble averages of the driving force along the coordinate λ . The relation in Equation 4 is valid for any $H(\lambda)$ and is not restricted to any particular form (for example, Equation 1). This general validity is a very important feature, because it gives us the freedom and flexibility to choose any quasistatic process that is convenient for our purposes.

Equation 4 provides a fundamental recipe for the measurement of free-energy differences using equilibrium simulations. It relies on the numerical evaluation of W_{qs} by the construction of a sequence of equilibrium states along a quasistatic process between the system of interest and the reference system. The ensemble averages of the driving force are evaluated at several values on the interval $[\lambda_1, \lambda_2]$ using a Monte Carlo or molecular dynamics sampling algorithm, after which the integration is carried out by standard numerical techniques. Several detailed examples of practical applications of this approach can be found in the book by Daan Frenkel and Berend Smit.²

Although this approach is very flexible and involves no approximations, it has one major drawback. To obtain an accurate estimate of W_{qs} , the ensemble averages of the driving force need to be evaluated on a sufficiently dense mesh of

equilibrium states along a quasistatic process. Because each state requires a separate equilibrium simulation, this procedure involves significant computational effort.

There exist equilibrium methods that are less demanding. Two examples are the histogram⁸ and cumulant expansion⁹ techniques, which allow the calculation of free-energy differences from a single equilibrium simulation by manipulating an energy histogram recorded during the simulation. However, the accuracy of these approaches is limited because these manipulations are sensitive to the relatively poor sampling of the high and low energy tails of the histogram and the truncation of the infinite cumulant expansion. In this sense, the “exact” thermodynamic-integration scheme is more robust, although one pays a price through its high computational cost.

Nonequilibrium measurement of quasistatic work

A computationally efficient alternative to the costly equilibrium measurement of W_{qs} is based on replacing the quasistatic sequence of equilibrium states by a dynamical sequence of *nonequilibrium* states. This can be achieved by introducing a time-dependent element into the originally static sequence of states. We can do so by making $\lambda = \lambda(t)$ an explicit function of the “time” t so that λ changes dynamically during the simulation. The “time” t should not be always interpreted as a real time. For example, in contrast with molecular dynamics, the Metropolis Monte Carlo scheme does not involve a natural time scale, so that t is simply an index variable that orders the sequence of sampling operations, measured in simulation steps.

Suppose we choose $\lambda(t)$ such that $\lambda(0) = \lambda_1$ and $\lambda(t_{\text{sim}}) = \lambda_2$, so that λ changes monotonically from λ_1 to λ_2 in a time t_{sim} . Accordingly, the Hamiltonian $H(\lambda) = H(\lambda(t))$ also becomes a function of t and changes from the initial system $H(\lambda_1)$ to the final system $H(\lambda_2)$ in the same time. The *dynamical* work W_{dyn} done by the driving force along this process, defined as

$$W_{\text{dyn}} = \int_0^{t_{\text{sim}}} dt \frac{d\lambda}{dt} \frac{\partial H}{\partial \lambda} \quad (5)$$

provides an estimator for the work W_{qs} done along the quasistatic process between the systems $H(\lambda_1)$ and $H(\lambda_2)$.

The point of this procedure is that W_{dyn} can be found from a single simulation, because the integration in Equation 5 involves *instantaneous* values of $\partial H/\partial \lambda$ instead of ensemble averages. Thus, this procedure would be much less costly than the evaluation of W_{qs} by the thermodynamic-integration procedure in Equation 4. There is, of course, a

trade-off. Although the thermodynamic-integration method is inherently “exact” in that the errors are associated only with statistical sampling and the discreteness of the mesh used for the numerical integration, the dynamical work procedure provides a *biased* estimate for W_{qs} . That is, aside from statistical errors, the dynamical estimator W_{dyn} is subject to a systematic error ΔE_{sys} . Both types of error are due to the nonequilibrium or irreversible nature of the dynamical process.

The statistical errors originate from the fact that the value of the integral in Equation 5 depends on the initial conditions of the dynamical process. In other words, for an ensemble of different initial conditions and a given time t_{sim} , the value of W_{dyn} in Equation 5 is not unique. Instead, it is a statistical quantity characterized by a distribution function with a finite variance.

The systematic error arises from the fact that the mean of the dynamical work distribution is shifted with respect to the value of the ideal quasistatic work W_{qs} . This shift is caused by the dissipative entropy production characteristic of irreversible processes. Because the entropy will always increase, the systematic error ΔE_{diss} is always positive, so that the average value $\overline{W}_{\text{dyn}}$ of many measurements of the dynamical work is an upper bound to the work W_{qs} along the corresponding quasistatic process:

$$\overline{W}_{\text{dyn}} = W_{\text{qs}} + \Delta E_{\text{diss}}. \quad (6)$$

The only exception is for the limiting case where $t_{\text{sim}} \rightarrow \infty$ and the transformation from $H(\lambda_1)$ to $H(\lambda_2)$ becomes infinitely slow. Only in this case does the dynamical process become ideally quasistatic and reversible; there is no dissipation, and a measurement of W_{dyn} will yield the exact value W_{qs} .

Figure 1 shows typical statistical distributions of nonequilibrium measurements W_{dyn} for three different values of t_{sim} : two finite values t_1 and t_2 with $t_1 < t_2$, and the adiabatic case $t_{\text{sim}} \rightarrow \infty$. For the latter, the distribution function is a Dirac delta function with zero variance and a mean that coincides exactly with W_{qs} . For finite t_{sim} the typical distribution is approximately Gaussian with a finite variance and its mean shifted with respect to W_{qs} by ΔE_{diss} . For shorter t_{sim} , both the statistical and systematic errors increase because of greater irreversibility and dissipation.

These errors seem to pose a very serious limitation to the application of this approach in practical situations, because computer time is always finite, and it is impossible to reach anywhere near the adiabatic limit $t_{\text{sim}} \rightarrow \infty$. Fortunately, in

practice the convergence of the finite-width distribution toward the ideal delta function is remarkably rapid. Both systematic and statistical errors decay rapidly with increasing t_{sim} , and accurate estimations of W_{qs} can be made using relatively short simulations, whose length is comparable to that of a typical equilibrium Monte Carlo or molecular dynamics simulation. Moreover, the systematic error caused by the dissipation can be estimated in a relatively simple fashion. This estimation can be done by exploiting the fact that the systematic error is always positive. Because of this property we can find upper and lower bounds for the exact W_{qs} by performing dynamical simulations in both directions.¹⁰ For example, when we simulate a process in which λ starts at λ_1 and ends at λ_2 , we measure the estimator

$$\overline{W}_{\text{dyn}}(1 \rightarrow 2) = W_{\text{qs}} + \Delta E_{\text{diss}}(1 \rightarrow 2) \quad (7)$$

which provides an upper bound to W_{qs} . But if we invert the direction of this process by starting at λ_2 and ending at λ_1 , we find the estimator

$$\overline{W}_{\text{dyn}}(2 \rightarrow 1) = -W_{\text{qs}} + \Delta E_{\text{diss}}(2 \rightarrow 1) \quad (8)$$

which provides an upper bound for $-W_{\text{qs}}$. Consequently, the estimator $-\overline{W}_{\text{dyn}}(2 \rightarrow 1)$ establishes a lower bound for $+W_{\text{qs}}$. In this way, we can systematically determine error bars and evaluate the accuracy of the results obtained with the nonequilibrium approach.

The reversible-scaling method

Based on this nonequilibrium approach, we have recently developed the reversible-scaling method for efficient free-energy calculations.¹ The method relies on the dynamical simulation of a specific quasistatic process in which the coordinate λ is used to scale the potential-energy function of the system of interest. This particular process allows us to estimate the free energy of a physical system as a function of temperature, using only one constant temperature dynamical simulation. The method represents a significant efficiency gain compared to the case where only one free-energy value is obtained per quasistatic process. For example, for the coupled Hamiltonian in Equation 1, only the initial and final states represent physically relevant states, which means that the information gathered at the intermediate states of the process has no physical meaning and serves only to connect the end points, yielding only one relevant free-energy difference per process.

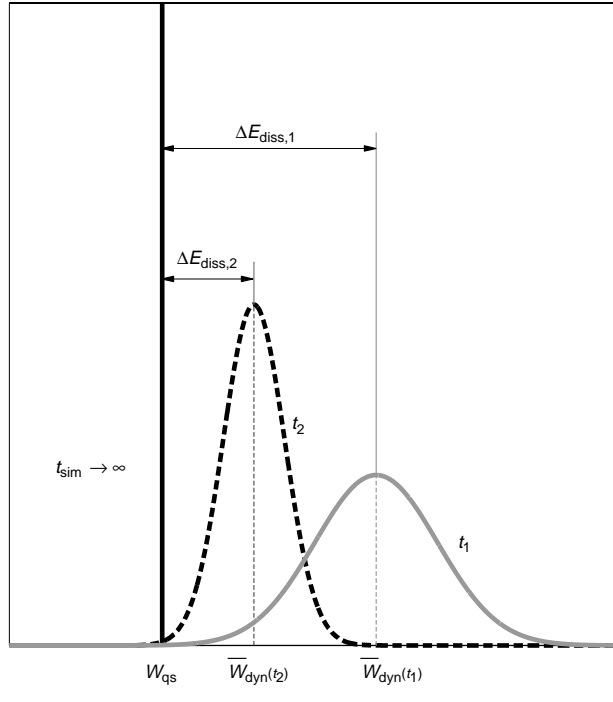


Figure 1. Typical statistical distribution functions for nonequilibrium measurements W_{dyn} for three different values of t_{sim} . For $t_{\text{sim}} \rightarrow \infty$ the process is ideally quasistatic and the distribution is a Dirac delta function centered at the quasistatic work W_{qs} (black curve). For the finite values t_1 and t_2 , with $t_1 < t_2$, the distribution functions are approximately Gaussian with a finite variance and their mean shifted with respect to W_{qs} by a systematic error ΔE_{diss} . For t_1 , both the statistical and systematic errors are greater than for t_2 owing to greater irreversibility and dissipation.

For the reversible-scaling process, the situation is different because all states along the process represent physically relevant states. More specifically, each state along this process corresponds to the physical system of interest at a unique temperature. In this manner, all free-energy differences along the process are physically meaningful, and the free energies of all these states can be estimated from one dynamical simulation.

To see how the method works, consider a classical N -particle system described by the Hamiltonian

$$H_0 = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (9)$$

where \mathbf{r}_i and \mathbf{p}_i are the position and momentum vectors of particle i , and U_0 is the potential energy describing the interactions between them. We assume that the system is in thermal equilibrium with a heat bath at temperature T_0 and confined to a fixed volume V . From the canonical partition function, we find that the Helmholtz free energy is given by²

$$F_0(T_0) = -k_B T_0 \ln \left[\int_V d^{3N} r \exp(-U_0/k_B T_0) \right] + 3Nk_B T_0 \ln \Lambda(T_0) \quad (10)$$

where $\Lambda(T_0) = (h^2/2\pi m k_B T_0)^{1/2}$ is the thermal de Broglie wavelength. The two terms in Equation 10 represent the configurational and ideal gas parts of the free energy, respectively.²

Now consider the scaled system H_{sc} , which is constructed from H_0 by introducing the scaling factor $\lambda > 0$ in the potential energy function:

$$H_{sc}(\lambda) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \lambda U_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (11)$$

In the same manner as we did for H_0 , we can write down the partition function and find that its free energy is given by

$$F_{sc}(\lambda, T_0) = -k_B T_0 \ln \left[\int_V d^{3N} r \exp(-U_0/k_B T) \right] + 3Nk_B T_0 \ln \Lambda(T_0) \quad (12)$$

where we have rewritten the Boltzmann factor $\exp(-\lambda U_0/k_B T_0)$ as $\exp(-U_0/k_B T)$ by introducing

$$T = T_0/\lambda. \quad (13)$$

If we look carefully at Equations 10 and 12, we see that if we replace T_0 by T in Equation 10, the configurational integrals in both expressions become equal. In this manner, it follows that $F_0(T)$ and $F_{sc}(\lambda, T_0)$ are related according to

$$\frac{F_0(T)}{T} = \frac{F_{sc}(\lambda, T_0)}{T_0} + \frac{3}{2} Nk_B \ln \frac{T_0}{T}. \quad (14)$$

This relation means that the problem of calculating the free energy of H_0 as a function of temperature is completely equivalent to determining the free energy of the scaled system H_{sc} as a function of λ at a fixed temperature T_0 .

This latter problem can be tackled very efficiently using the nonequilibrium approach discussed previously. The idea is to estimate the function $F_{sc}(\lambda, T_0)$ at a fixed temperature T_0 by calculating dynamical estimates for free-energy differences along the sequence of states of the scaling process defined by Equation 11. To do so, we choose one reference state $\lambda = \lambda_{ref}$ along this path for which the free energy

$F_{sc}(\lambda_{ref}, T_0) \equiv F_{ref}$ is known beforehand. We can then write

$$F_{sc}(\lambda, T_0) = F_{ref} + W_{qs}(\lambda) \quad (15)$$

where

$$W_{qs}(\lambda) = \int_{\lambda_{ref}}^{\lambda} d\lambda' \langle U_0 \rangle_{\lambda'} \quad (16)$$

represents the work done along the quasistatic process between the reference state and the state λ at a fixed temperature T_0 . It is important to emphasize that the function $W_{qs}(\lambda)$ is physically meaningful for any value of λ .

Using the nonequilibrium approach discussed in the previous section, we can obtain an estimator for the function $W_{qs}(\lambda)$. For this purpose we perform a simulation in which the coordinate $\lambda = \lambda(t)$ varies dynamically along the simulation. For example, if we start in the reference state, $\lambda(0) = \lambda_{ref}$ and reach the final state, $\lambda(t_{sim}) = \lambda_{final}$, in a time t_{sim} , we can evaluate the dynamical cumulative work function

$$W_{dyn}(t) = \int_0^t dt' \frac{d\lambda}{dt'} \bigg|_{\lambda'} U_0(\mathbf{r}_1(t'), \dots, \mathbf{r}_N(t')) \quad (17)$$

by numerically accumulating the integral during the simulation. In this manner we have estimators for the function $W_{qs}(\lambda)$ in the scaling coordinate interval $[\lambda_{ref}, \lambda_{final}]$. In a practical simulation, this function is discretized in terms of simulation steps, so that the estimators are found on a discrete mesh on the scaling coordinate interval. Obviously, this mesh will become denser with increasing t_{sim} , as more simulation steps are required to cover a specified scaling coordinate interval.

From Equation 15, the results for $W_{qs}(\lambda)$ immediately provide us with estimators for the function $F_{sc}(\lambda, T_0)$ on the same interval. Finally, by Equations 13 and 14, we find the free energy $F_0(T)$ of the physical system H_0 on the temperature interval $[T_0/\lambda_{ref}, T_0/\lambda_{final}]$.

This process is illustrated schematically in Figure 2, where the dynamical work function $W_{dyn}(t)$ accumulated during the scaling simulation undergoes three transformations to yield the free energy of the physical system H_0 as a function of temperature. First, the function $\lambda(t)$ is used to transform the function $W_{dyn}(t)$ on the time step interval $[0, t_{sim}]$ into the estimator for the function $W_{qs}(\lambda)$ on the corresponding scaling coordinate interval $[\lambda_{ref}, \lambda_{final}]$. Then, using Equation 15, this result is transformed to yield the function $F_{sc}(\lambda, T_0)$ on the same interval. The last step involves a transformation based on Equations 13 and 14 leading to the desired func-

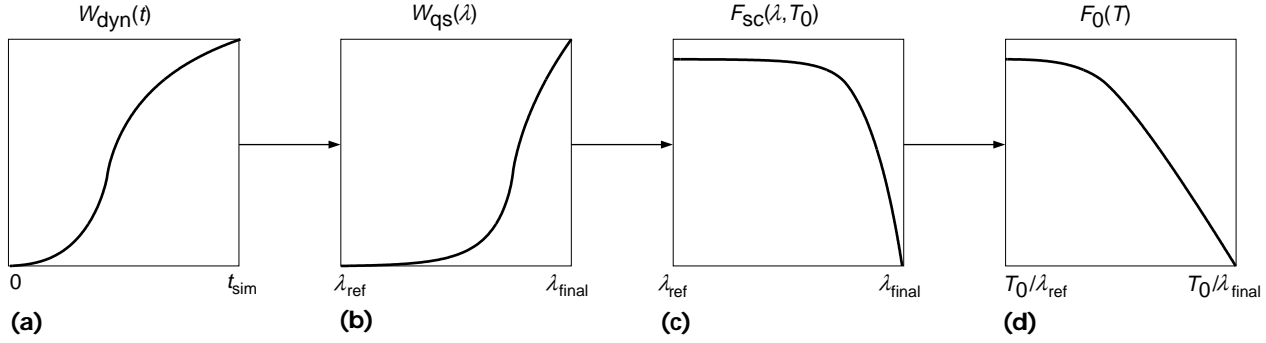


Figure 2. Schematic representation of the three steps that transform the function $W_{\text{dyn}}(t)$ on the time interval $[0, t_{\text{sim}}]$ into the desired $F_0(T)$ on the temperature interval $[T_0/\lambda_{\text{ref}}, T_0/\lambda_{\text{final}}]$. The first step transforms (a) the function $W_{\text{dyn}}(t)$ on the interval $[0, t_{\text{sim}}]$ into (b) estimators for $W_{\text{sq}}(\lambda)$ on the scaling coordinate interval $[\lambda_{\text{ref}}, \lambda_{\text{final}}]$, using the function $\lambda(t)$. The second step involves the transformation of $W_{\text{sq}}(\lambda)$ into (c) $F_{\text{sc}}(\lambda, T_0)$, using Equation 15. Finally, using Equations 13 and 14, the function $F_{\text{sc}}(\lambda, T_0)$ on the interval $[\lambda_{\text{ref}}, \lambda_{\text{final}}]$ is mapped onto (d) the desired function $F_0(T)$ on the temperature interval $[T_0/\lambda_{\text{ref}}, T_0/\lambda_{\text{final}}]$.

tion $F_0(T)$ on the temperature interval $[T_0/\lambda_{\text{ref}}, T_0/\lambda_{\text{final}}]$.

Of course, the measurement of the dynamical work function $W_{\text{dyn}}(t)$ from a single simulation is subject to the statistical and systematic errors caused by the irreversible dissipation. These errors will also appear in the final values obtained for $F_0(T)$. But the magnitude of these errors usually decays rapidly with increasing t_{sim} (for a fixed scaling factor interval), so that accurate measurements of $F_0(T)$ can be achieved using simulations whose length is of the order of a typical equilibrium simulation. Moreover, the errors can be estimated explicitly by the procedures discussed in the previous section.

Application to the 2D Ising model

Let us now see how we can implement this procedure. For this purpose, we will apply the Metropolis Monte Carlo algorithm and the reversible-scaling technique to determine the free energy as a function of temperature for the Ising model on a square lattice. Because the analytical solution to this system is known,¹¹ we will be able to compare our numerical results to exact values.

The Ising model is described by the Hamiltonian

$$H_0[\mathbf{z}] = -J \sum_{\langle i, j \rangle} \sigma_i \sigma_j \quad (18)$$

where $\mathbf{z} = \{\sigma_1, \sigma_2, \dots, \sigma_N\}$ represents a configuration of N spins arranged on an $L \times L$ square lattice. Each spin has a value of ± 1 , and interacts only with its four nearest neighbors, as indicated by the summation over all nearest-neighbor pairs $\langle i, j \rangle$. The interaction energy between the spins is $-J$. We impose periodic boundary conditions to avoid boundary effects. Note that the energy is purely configurational. Because there is no kinetic energy part, the kinetic energy contribution in the reversible-scaling relation in Equation 14, represented by the logarithmic term, should be omitted in this application.

To implement the reversible-scaling method, we need to simulate the scaled system

$$H_{\text{sc}}[\mathbf{z}, \lambda] = -\lambda J \sum_{\langle i, j \rangle} \sigma_i \sigma_j \quad (19)$$

at some constant temperature T_0 . We can do this using the standard single-flip Metropolis Monte Carlo algorithm,²⁻⁵ where the acceptance probabilities $P_{\text{flip}} = P_{\text{flip}}(\lambda)$ depend explicitly on the value of the scaling coordinate λ .

The reversible-scaling process is simulated by generating a series of spin configurations while the scaling variable λ is varying dynamically between its initial and final values. The simulation consists of repeatedly executing the following Monte Carlo “time” step, which consists of two parts. First, a new spin configuration is generated from the previous one by doing a Metropolis “sweep” through the entire system, attempting to flip each of the N spins using the acceptance probabilities corresponding to the current value of λ . After this sweep the values of the scaling coordinate λ and the corresponding acceptance probabilities $P_{\text{flip}}(\lambda)$ are updated for generating the next system configuration.

This procedure is then repeated for t_{sim} steps, until the scaling variable has evolved from its initial to its final value. In this way, the configurations \mathbf{z} and the scaling variable λ evolve according to a series of discrete steps

$$\mathbf{z}(t) \rightarrow \mathbf{z}(0), \mathbf{z}(1), \dots, \mathbf{z}(t_{\text{sim}}) \quad (20)$$

and

$$\lambda(t) \rightarrow \lambda(0), \lambda(1), \dots, \lambda(t_{\text{sim}}) \quad (21)$$

where t runs from 0 to t_{sim} .

The work accumulated during each step is calculated as follows. Suppose a spin configuration $\mathbf{z}(t)$ was generated using the acceptance probabilities corresponding to the scaling

Suggestions for further study

An interesting aspect of the reversible-scaling technique is the dissipation along the simulated nonequilibrium processes. In this column we have discussed how these effects, which appear in the form of statistical and systematic errors, may be estimated in practice. It is insightful to look at these effects for the 2D Ising model.

1. Repeat the reversible-scaling simulations for the Ising model on a square lattice. Choose $L = 100$, $T_0 = 1$, $J = 1$, and $k_B = 1$. Instead of starting the process in the reference state $\lambda(0) = 0$, initiate the scaling process at $\lambda(0) = 1$. Use the function

$$\lambda(t) = 1 - \frac{t}{t_{\text{sim}}}$$

so that the scaling coordinate decreases linearly from 1 to 0 in t_{sim} steps. Consider $t_{\text{sim}} = 10^3$, 10^4 , and 10^5 , and compare the results to the analytical data and the reversible-scaling results obtained using the processes that start at $\lambda = 0$. To obtain the values for the exact solution, you may use the C++ code available at mmm.mit.edu/cise/2dising. What is the difference between the results obtained in the two directions?

2. Evaluate the magnitude of the statistical fluctuations for $t_{\text{sim}} = 10^5$ by running 50 scaling simulations based on independent initial conditions. Do this for both directions and look at how the statistical error evolves as a function of temperature. Do you find a maximum for the statistical error? Explain the physical origin of this maximum. Is there a difference between the systematic errors for the two directions? Give a physical explanation for this difference.
3. In principle, we may use any functional form of $\lambda(t)$. However, the functional form of $\lambda(t)$ affects the dissipation along a nonequilibrium simulation.¹ In fact, based on the fluctuation-dissipation theorem of statistical mechanics, one can derive a formula for the systematic

error accumulated along the simulation of a nonequilibrium process.^{2,3} For the reversible-scaling process this relation is

$$\Delta E_{\text{diss}} = T_0 \int_0^{t_{\text{sim}}} dt \left(\frac{d\lambda(t)}{dt} \right)^2 \tau(t) C(\lambda(t)) \quad (\text{A})$$

where $\tau(t)$ represents the characteristic correlation time for the fluctuations in the generalized force, and $C(\lambda)$ is the specific heat of the scaled system $H(\lambda)$ at temperature T_0 .

Given the relation in Equation A, try the alternative switching function

$$\lambda(t) = \left(\frac{t}{t_{\text{sim}}} \right)^5 \quad (\text{B})$$

and perform reversible-scaling simulations starting at the reference state $\lambda(0) = 0$. Is this function better than the linear one? Why? Think of a way to design an optimal function that would minimize the dissipation.

4. Compare the computational cost of the reversible-scaling technique to the thermodynamic integration method. For this purpose, perform a set of independent equilibrium simulations for several fixed values of λ between 0 and 1 at a temperature T_0 , and integrate the ensemble averages of the driving force using a numerical-integration method such as Gaussian quadrature.

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coordinate $\lambda(t)$ associated with step t . After the generation of this configuration, the value of λ will be updated to its new value $\lambda(t+1)$. As a result, the energy of configuration $\mathbf{z}(t)$ will change by an amount $\Delta W = H_{\text{sc}}[\mathbf{z}(t), \lambda(t+1)] - H_{\text{sc}}[\mathbf{z}(t), \lambda(t)] = [\lambda(t+1) - \lambda(t)] H_0[\mathbf{z}(t)]$, which is equal to the work done by the instantaneous driving force acting on configuration $\mathbf{z}(t)$. By accumulating these differences along the series of time steps, we build up the cumulative dynamical work function $W_{\text{dyn}}(t)$ for all t between 0 and t_{sim} according to

$$W_{\text{dyn}}(0) = 0 \quad (22)$$

and

$$W_{\text{dyn}}(t) = \sum_{n=1}^t [\lambda(n) - \lambda(n-1)] H_0[\mathbf{z}(n-1)] \quad (23)$$

with $t = 1, \dots, t_{\text{sim}}$.

An implementation of this procedure is given in the following algorithm:

1. Generate an initial condition $\mathbf{z}(0)$ for the reversible-scaling process by running Nequil equilibration Metropolis sweeps with the initial acceptance probabilities $P_{\text{flip}}(\lambda(0))$.
2. Set $t = 0$ and $W_{\text{dyn}}(t) = 0$.
3. Accumulate the dynamical work: $W_{\text{dyn}}(t+1) = W_{\text{dyn}}(t) + [\lambda(t+1) - \lambda(t)] H_0[\mathbf{z}(t)]$.

4. Increment t by one: $t = t + 1$.
5. If $t < t_{\text{sim}}$, then continue with Step 6; otherwise the process is complete.
6. Compute the new acceptance probabilities $P_{\text{flip}}(\lambda(t))$.
7. Perform one Metropolis sweep with the new acceptance probabilities to generate a new configuration $\mathbf{z}(t)$.
8. Repeat from Step 3.

This algorithm will give us the values of the dynamical work function $W_{\text{dyn}}(t)$ on the time interval $[0, t_{\text{sim}}]$, yielding the curve shown in Figure 2a. The function $F_0(T)$ can now be found, without any further simulations, by applying the three transformations shown in Figures 2b, 2c, and 2d.

We have used this algorithm to compute the free energy as a function of temperature for a 100×100 Ising system with the interaction energy $J = 1$. We chose the initial value of the scaling coordinate to coincide with the reference state $\lambda(0) = \lambda_{\text{ref}} = 0$. For this value the scaled system corresponds to a collection of noninteracting spins, for which the free energy at the simulation temperature T_0 is simply (setting $k_B = 1$)

$$F_{\text{ref}} = F_{\text{sc}}(\lambda_{\text{ref}}, T_0) = -100^2 T_0 \ln 2 \quad (24)$$

because the internal energy is zero (no interactions among the spins) and the entropy per spin equals $\ln 2$. The final value of the scaling coordinate and the simulation temperature T_0 were chosen to be equal to one: $\lambda(t_{\text{sim}}) = \lambda_{\text{final}} = 1$ and $T_0 = 1$. In this way, by Equation 13, the scaling factor interval $\lambda \in [0, 1]$ corresponds to the temperature interval $T \in [1, \infty)$ in the system of interest. With this choice, we cover a temperature interval that includes the critical temperature $T_c \approx 2.27$, at which the infinite Ising system on a square lattice undergoes a continuous phase transition. Although our system is finite, the existence of this phase transition is signaled by a sharp peak in the specific heat, which manifests itself in a rapid change of the derivative of the free energy with respect to temperature.

For simplicity we have chosen the functional form of $\lambda(t)$ to be

$$\lambda(t) = t/t_{\text{sim}}$$

so that the scaling coordinate λ increases linearly from 0 to 1 in t_{sim} steps. The method is by no means restricted to this particular form, and in principle we may use any monotonic function $\lambda(t)$ that satisfies the boundary conditions $\lambda(0) = 0$ and $\lambda(t_{\text{sim}}) = 1$. However, the specific form of this function affects the magnitude of the dissipation along the nonequi-

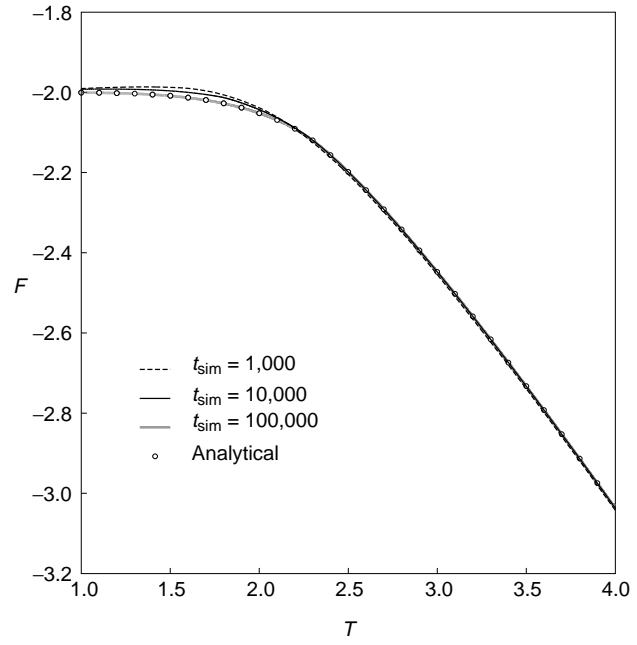


Figure 3. Free energy per spin as a function of temperature for the 100×100 square Ising model. The three curves represent results obtained with the reversible-scaling method for $t_{\text{sim}} = 10^3$ (dashed curve), $t_{\text{sim}} = 10^4$ (black curve), and $t_{\text{sim}} = 10^5$ (gray curve). Black circles represent analytical values.¹¹

librium simulation (see Problem 3 in the sidebar, “Suggestions for further study”).

Figure 3 shows the results of three different reversible-scaling simulations for the free energy per spin as a function of temperature using a total number of $t_{\text{sim}} = 10^3$, 10^4 , and 10^5 time steps. These results correspond to the dashed, black, and gray curves, respectively. The curves appear to be continuous because each step yields a free-energy value for a different temperature.

Each curve represents only one nonequilibrium simulation so that the results have not been corrected for the systematic errors caused by the dissipation, nor have estimates been made for statistical fluctuations. The circles denote the exact values for the 100×100 system obtained from the analytical solution reported by A.E. Ferdinand and M.E. Fisher.¹¹

We see that the convergence of the reversible-scaling data to the exact solution is remarkably rapid. For $t_{\text{sim}} = 10^3$, which is a very short simulation, the agreement is already reasonable for temperatures above T_c . However, as the scaling simulation crosses the critical region, the errors start increasing and the deviation from the exact values becomes relatively large. For $t_{\text{sim}} = 10^4$ the result improves considerably. For $T > T_c$ the reversible-scaling results are essentially identical to the exact results, while the deviations for $T < T_c$ have decreased significantly. A further increase of t_{sim} to 10^5 steps, which is still relatively short, yields a reversible-scaling curve that provides a “perfect” fit to the analytical data over the entire temperature range. It is remarkable that even without

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carrying out an explicit estimation of systematic and statistical errors, the reversible-scaling results agree very well with the exact solution. This agreement is an indication that the displaced finite-width Gaussian distribution function of non-equilibrium measurements converges quite fast, as both the statistical and systematic errors decay rapidly. We may conclude that the reversible-scaling technique provides an efficient calculation scheme in that a single nonequilibrium simulation, whose length is of the order of one typical equilibrium Monte Carlo simulation, gives accurate results for the free energy as a function of temperature.

Ever since the early stages of the development of the reversible-scaling technique, its simplicity and effectiveness have been remarkable. The fact that one is able to accurately calculate the free energy over an entire temperature range using only one relatively short scaling simulation is further indication of the richness of information inherent in atomistic simulations. Based on the results obtained in our investigations so far, we believe that the nonequilibrium approach—in particular, the reversible-scaling technique—provides a useful alternative to the well-established equilibrium approaches to calculations of the free energy. \square

Acknowledgments

Maurice de Koning gratefully acknowledges support from the Brazilian agency Fundação de Amparo à Pesquisa do Estado de São Paulo under Contract 97/14290-6. Wei Cai acknowledges support from the Lawrence Livermore National Laboratory. Alex Antonelli gratefully acknowledges support from the Brazilian funding agencies FAPESP, CNPq, and FAEP. Sidney Yip acknowledges support from AFOSR Grant

F49620-96-1-0447 and from the Lawrence Livermore National Laboratory. We thank the editors, Harvey Gould and Jan Tobochnik, for their helpful comments and suggestions.

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