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Optimized Free-Energy Evaluation Using a Single Reversible-Scaling Simulation

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We present a method, for highly efficient free-energy calculations by means of molecular dynamics and Monte Carlo simulations, which is an optimized combination of coupling parameter and adiabatic switching formalisms. This approach involves dynamical reversible scaling of the potential energy function of a system of interest, and allows accurate determination of its free energy over a wide temperature interval from a single simulation. The method is demonstrated in two applications: crystalline Si at zero pressure and a fcc nearest-neighbor antiferromagnetic Ising model.

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In the study of thermodynamic properties of materials [1,2], free-energy calculation is a unique application of computer simulation techniques. For this purpose, the coupling parameter formalism [2,3] provides a powerful and robust framework which underlies state-of-the-art techniques such as thermodynamic integration (TI) [2] and adiabatic switching (AS) [4–10]. Standard application of this approach involves the evaluation of reversible work along a path connecting a physical system of interest to a reference. Usually, the path is constructed using a composite Hamiltonian $H(\lambda)$ coupling the two systems through a parameter λ. Upon varying λ the coupled system evolves along a reversible trajectory, changing continuously from the system of interest to the reference. The reversible work done by the generalized force $\partial H/\partial\lambda$ along this path is then equal to the free-energy difference between the systems. While this approach is very powerful, it is not optimal in that *only* the initial and final points on the trajectory correspond to physically relevant systems. The information gathered at the intermediate states of the path has no physical meaning, serving only to connect the end points of the path. As a consequence, one obtains only one value of the desired free energy per simulation.

In this Letter we describe a formulation which fully utilizes all the information available along a reversible path and thereby allows the evaluation of free energies over a wide temperature interval from a single simulation. This approach, which effectively exploits both the coupling parameter formalism and the adiabatic switching technique, is based on the use of a specific path which is defined by the introduction of a scaling factor λ in the potential energy function of the physical system of interest. The fundamental difference from the usual coupling approach is that for this particular path *all* intermediate states provide physically relevant information. In fact, an exact relation between the partition functions of the original and the scaled systems shows that all the states along the scaling path correspond to the original physical system at different temperatures. The combination of this reversible-scaling concept with the dynamical variation of λ within the adiabatic switching method results in a highly optimized technique with a significant efficiency gain without loss of accuracy.

The idea of determining free energies as a function of a thermodynamic variable from a single simulation is not new, as several simulation methods designed for this purpose have been developed during the last decade. Important examples include histogram analysis methods, the cumulant expansion approach, and the method for direct evaluation of the density of states. The histogram [11,12] and cumulant expansion [13,14] methods are based on the construction of a histogram measuring energy probability densities from a simulation performed at a single value of the thermodynamic variable of interest. The results can then be extended to other values by appropriate reweighing of the original histogram and use of a truncated generalized cumulant expansion, respectively. Unfortunately, the range over which the thermodynamic variable can be covered accurately is limited due to poor sampling of the high and low energy tails of the original energy histogram and the truncation of the infinite cumulant expansion. The direct density of states technique [15] enables the calculation of free energies as a function of a thermodynamic variable by analyzing the configurations generated during a single simulation. While this approach has shown to be efficient and accurate for discrete systems such as the Ising spin model, its application to systems characterized by continuous interactions is far from straightforward.

The reversible-scaling technique presented here provides a notable alternative to these methods since, aside from its efficiency, it does not rely on any uncontrollable approximations and provides accurate results over a wide temperature range. Moreover, the approach appears to be applicable to a wide range of physical systems, and its implementation in a molecular dynamics (MD) or Monte Carlo (MC) code is straightforward. To demonstrate these features we calculate the free energy of two systems characterized by rather different interactions: single crystal Si described by a continuous empirical potential and a fcc nearest-neighbor antiferromagnetic Ising system.

Let the system of interest, consisting of N particles of equal mass m, be described by the Hamiltonian

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

where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and momentum vectors of particle i, and U_0 is the potential energy function. It is assumed that the system is in thermal equilibrium with a heat bath at temperature T_0 and confined to a fixed volume V. The Helmholtz free energy is given by

$$F_0(T_0) = -k_B T_0 \ln\left[\int_V d^{3N}r \exp(-U_0/k_B T_0)\right] + 3Nk_B T_0 \ln\Lambda(T_0), \tag{2}$$

where k_B is Boltzmann's constant and $\Lambda(T_0)$ is the thermal de Broglie wavelength $(h^2/2\pi m k_B T_0)^{1/2}$.

Now consider the scaled system H_1 which is constructed from H_0 by introducing a scaling factor $\lambda > 0$ in the potential energy function,

$$H_1(\lambda) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \lambda U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N). \tag{3}$$

The corresponding free energy is

$$F_1(T_0, \lambda) = -k_B T_0 \ln\left[\int_V d^{3N}r \exp(-U_0/k_B T)\right] + 3Nk_B T_0 \ln\Lambda(T_0), \tag{4}$$

where T is related to T_0 and λ as

$$T = \frac{T_0}{\lambda}. \tag{5}$$

Considering Eqs. (2), (4), and (5) it follows that the temperature dependence of $F_0(T)$ is directly related to the λ dependence of $F_1(\lambda, T_0)$ at *fixed* temperature T_0,

$$\frac{F_0(T)}{T} = \frac{F_1(T_0, \lambda)}{T_0} + \frac{3}{2} N k_B \ln\frac{T_0}{T}. \tag{6}$$

Thus, the problem of calculating $F_0(T)$ for system H_0 is completely equivalent to the problem of evaluating $F_1(T_0, \lambda)$ as a function of λ for the scaled system $H_1(\lambda)$.

Problems of the latter type can be addressed very efficiently and accurately using the AS technique [4–10]. In principle, this method allows the determination of the free-energy dependence on an external parameter in a Hamiltonian of interest from a single MD or MC simulation, without relying on any uncontrollable approximations. Since the calculation of $F_0(T)$ of physical system H_0 can be formulated in such terms through (6), it is possible to obtain $F_0(T)$ indirectly through the determination of $F_1(T_0, \lambda)$ by an AS simulation of the scaled system $H_1(\lambda)$. This approach fully benefits from the efficiency and accuracy of AS and, as will be demonstrated in the applications, provides a very powerful tool for the calculation of free energies as a function of temperature.

Our approach is to calculate $F_1(T_0, \lambda)$ by exploiting the AS technique for estimating the reversible work associated with processes in which λ is varied adiabatically at a fixed temperature. Such processes are simulated by means of a MD or MC run of system $H_1(\lambda)$ at temperature T_0 where the parameter $\lambda = \lambda(t)$ is a function of time t (or MC step) that varies continuously between $\lambda(0)$ and $\lambda(t_s)$. Here, the switching time t_s represents the total length of the AS process, measured in time (or MC) steps. If the simulated process is ideally adiabatic, the cumulative free-energy difference $\Delta F_1(\lambda(t), \lambda(0)) \equiv F_1(T_0, \lambda(t)) - F_1(T_0, \lambda(0))$ is equal to the cumulative reversible work $W(t)$ done by the generalized force $\partial H_1/\partial\lambda$ associated with λ,

$$\Delta F_1(\lambda(t), \lambda(0)) = \int_0^t dt' \left.\frac{d\lambda}{dt}\right|_{t'} U_0(\mathbf{r}_1(t'), \ldots, \mathbf{r}_N(t')) \equiv W(t). \tag{7}$$

Using (5) and (6), the time dependence of $W(t)$ can be linked to the temperature dependence of the free energy in H_0,

$$\frac{F_0(T(t))}{T(t)} = \frac{F_0(T(0))}{T(0)} + \frac{W(t)}{T_0} - \frac{3}{2} N k_B \ln\frac{T(t)}{T(0)}, \tag{8}$$

where $T(t) = T_0/\lambda(t)$ and $T(0) = T_0/\lambda(0)$. This result, which defines the approach that we call reversible scaling (RS), shows that *each* instant t along the AS simulation of system $H_1(\lambda)$ corresponds to the physical system H_0 at a *unique* temperature $T = T_0/\lambda(t)$. Thus, according to (8), the evaluation of the cumulative work function $W(t)$ along a *single* AS simulation of $H_1(\lambda)$ at constant temperature T_0 is sufficient to obtain the absolute free energy $F_0(T)$ on the temperature interval specified by the boundaries $T(0) = T_0/\lambda(0)$ and $T(t_s) = T_0/\lambda(t_s)$, provided that F_0 is known at one of these boundaries and the process is ideally reversible.

The requirement of knowing F_0 at one of the boundaries of the temperature interval is not a serious limitation since it is always possible to choose a suitable reference temperature for which the free energy can be evaluated using standard techniques. The second condition, however, might impose a more serious restriction on the practical applicability of RS since its satisfaction requires infinitely long switching times t_s. Obviously, this requirement cannot be strictly fulfilled in practical simulations where finite switching times are inevitable. The consequence of this is the introduction of irreversible energy dissipation along the process, in violation of Eq. (7). The work $W(t)$ is therefore not exactly equal to the free-energy difference, but only an upper limit estimate [7,9,10] which converges to the "exact" free-energy difference in the limit of using very long t_s. It has been shown, however, that in practice satisfactory convergence can be achieved using relatively short switching times [4–7,10]. Moreover, any small systematic errors caused by finite switching times can be estimated using a simple hysteresis analysis procedure [7,10].

It should also be noted here that the application of RS is not limited to the canonical ensemble discussed above. The methodology can be extended to other statistical ensembles such as the isobaric-isothermal ensemble by introducing appropriate modifications. Furthermore, we observe that the RS approach presented here is conceptually equivalent to the common procedure of integrating the appropriate free-energy derivative with respect to temperature [2]. The current approach is different, however, in that it is based on the coupling parameter formalism, which allows the determination of the free energy as a function of temperature from a single constant temperature AS simulation. In contrast, the common temperature integration procedure requires a number of independent simulations at different temperatures.

To illustrate the capabilities of RS we calculated the zero pressure Gibbs free energy of a single crystal of Si using MD simulations on a periodic cell of 512 atoms. U_0 was taken to be the environment-dependent interatomic potential (EDIP) model for Si [16], and the equations of motion of the isobaric-isothermal ensemble [17] utilized in the simulations were integrated using a time step of 0.2 fs. Both the simulation temperature T_0 and the reference temperature $T(0)$ were chosen at 200 K. The corresponding reference free energy was calculated using the quasiharmonic approximation [18]. The scaling factor $\lambda(t)$ in $H_1(\lambda)$ was set according to a linear interpolation between the initial and final values of λ, spanning the temperature interval between 200 and 1000 K in a switching time t_s.

Figure 1 shows the results of three different RS-MD simulations, characterized by switching times t_s of 0.1 ps, 1.0 ps, and 5.0 ps, respectively. Each curve shows the Gibbs free energy per atom, measured at a dense temperature grid along the corresponding RS-MD simulation. The circles correspond to a set of reference data obtained using an independent AS method in which interacting Si atoms are transformed into independent Einstein oscillators at selected temperatures [7].

These results clearly show the accuracy and efficiency of RS-MD. While the difference between the results obtained for $t_s = 0.1$ ps and the reference data is still relatively large for higher temperatures, the agreement is already within 0.1% over the whole temperature range for $t_s = 1.0$ ps and it is even better for $t_s = 5.0$ ps, where the RS-MD results are essentially identical to the reference data. It is important to point out here that the $t_s = 5.0$ ps simulation required only 2.5×10^4 MD steps for the evaluation of the *whole* free-energy curve, which required about 25 min of CPU time on a single SGI R10000 processor. In comparison, the data obtained with the reference method required of the order of 10^5 MD steps for *each* data point, so that the total computational cost associated with the entire reference data set was about a factor 36 higher than for the 5.0 ps RS-MD simulation.

As a second application we evaluate the configurational free energy as a function of temperature of a fcc nearest-neighbor antiferromagnetic Ising spin model at zero magnetic field [19]. This calculation is more challenging since the system shows a first order phase transformation in the temperature interval of interest, giving rise to

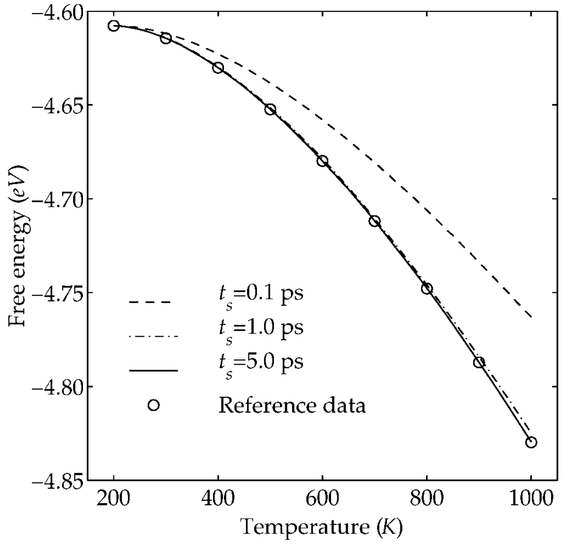

FIG. 1. Convergence of the RS-MD method for EDIP Si at zero pressure as a function of the switching time t_s, Gibbs free energy per atom obtained using three trajectories with switching times of 0.1, 1.0, and 5.0 ps, respectively. Circles represent reference data obtained using the independent reference AS method.

irreversible hysteresis effects. The system was simulated with a single flip Metropolis MC algorithm [20] using a computational cell containing 1728 spins subject to periodic boundary conditions. The RS-MC simulation was carried out at a (reduced) simulation temperature $T_0 = T(0) = 1$. The reference temperature was chosen at $T(t_s) = \infty$ for which the free energy per spin is known exactly: $F_0(T(t_s))/T(t_s) = -k_B \ln 2$. Similar to the RS-MD simulation of Si, the scaling factor $\lambda(t)$ was set according to a linear interpolation between the initial and final values of λ, spanning the temperature interval between $T = 1$ and $T = \infty$ in t_s RS-MC steps. Since only configurational contributions are of interest here, the kinetic contributions appearing in the form of the logarithmic terms in (6) and (8) were omitted.

Figure 2 shows the results of three different RS-MC simulations, characterized by switching times t_s of 1×10^3, 1×10^4, and 2×10^5 MCS, respectively. Each curve shows the configurational free energy per spin (in units of the nearest-neighbor interaction J) as a function of temperature, measured at a dense temperature grid along the corresponding RS-MC simulation. The circles with the error bars represent reference data obtained by standard thermodynamic integration of internal energies over the inverse temperature domain [19].

Despite the irreversible hysteresis effects caused by the first order phase transformation near $T \simeq 1.77$, RS-MC performs very well. For $T > 1.8$ the agreement is excellent for all three curves, while for lower temperatures the convergence is somewhat slower due to the occurrence of the phase transition during the switching process. However, "slower" is only a relative notion given that the lower temperature agreement between RS-MC and the reference data is already within 0.5% for $t_s = 2 \times 10^5$ MCS (about 30 min of CPU time). This is quite remarkable given the fact that the reference data were obtained from a set of 34 independent constant temperature simulations of 1×10^6 MCS per temperature. Accordingly, the total computational cost associated with this reference data set was about a factor 170 higher compared to the 2×10^5 MCS RS-MC simulation.

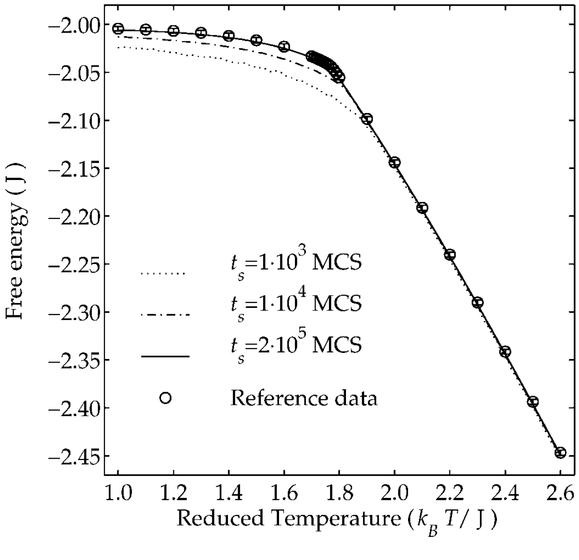

FIG. 2. Convergence of the RS-MC method for the fcc nearest-neighbor antiferromagnetic Ising spin model at zero field as a function of t_s, configurational free energy per spin (in units of the nearest-neighbor interaction J) obtained using three runs with 1×10^3, 1×10^4, and 2×10^5 MCS, respectively. Circles with error bars represent a set of reference data obtained using standard thermodynamic integration over the inverse temperature domain of the internal energy.

In both examples RS has shown to be substantially more efficient than the standard AS and TI approaches. In typical applications, the computational cost associated with RS should be of the order of a single simulation instead of a set of N runs utilized in standard AS and TI schemes, resulting in an efficiency gain that scales as N. We acknowledge that further exploration of the applicability of RS to physical systems more complex than the examples studied here would be worthwhile. We also note that the method, in particular, should be useful for free-energy calculations using computationally demanding modeling approaches such as tight-binding and first-principles molecular dynamics.

In conclusion, we have developed an effective method for calculating free energies as a function of temperature from a single MD or MC simulation. The essence of our approach lies in the simulation of a reversible-scaling path defined by the introduction of a scaling factor in the potential energy function of the physical system of interest. As demonstrated by the two different applications, the resulting method is accurate and very efficient. It appears that the method is generally applicable to a wide range of physical systems.

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