Direct Dynamical Calculation of Entropy and Free Energy by Adiabatic Switching

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If an ergodic Hamiltonian is changing slowly in time, its energy shell is an adiabatic invariant: Even though the energy changes, an initial surface of constant energy is mapped into a continuous family of surfaces, each of which is also of constant energy. This observation allows efficient and direct dynamical calculation of the entropy of classical fluids, exemplified here by a simple model of liquid water. The results depend substantially on the form of the "switching" function, suggesting possible improvements in traditional thermodynamic switching processes. Application of a similar adiabaticity to Nosé dynamics allows dynamical computation of differences in the Helmholtz free energy.

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Molecular dynamics (MD) and Monte Carlo (MC) simulations are important techniques for the study of classical and quantum many-body systems. These now standard simulation methods yield statistical information regarding properties that are explicit functions of the phase-space coordinates of a system, such as potential energy, temperature, and pressure. However, quoting from a recent critically reviewed reprint collection,[1] "By contrast, it is not in general possible to obtain directly from a simulation information on 'thermal' properties, i.e., quantities that depend on the total phase-space volume accessible to the system: examples include the entropy, Helmholtz free energy and chemical potentials." What is implied here is that rather than simply computing the time average of an explicit function of the dynamical variables, the thermodynamic definitions relating entropy and free-energy differences are mimicked computationally. For example, in the thermodynamic integration methods,[2,3] changes in the Helmholtz free energy A are determined from

$$\Delta A=\int_0^1\langle\Delta E\rangle_\lambda\,d\lambda\,, \tag{1}$$

where the integration "path" connecting the two states of interest must be thermodynamically reversible, and the equilibrium average $\langle\Delta E\rangle_\lambda$ must be sampled at a large enough number of values of λ to allow convergence of the integral. Even the "slow growth" method, which has more dynamical flavor, is derived from the same basis as thermodynamic integration.[4,5]

We present in this Letter the first realistic application, to molecular fluids, of an alternative method[6] for a computation of the entropy based on properties of the Hamiltonian dynamics lurking behind the usual MD method. The method presented uses, as in thermodynamic integration, a reference system, and the Hamiltonian is allowed to systematically evolve between the reference and the actual system of interest. The philosophical basis then changes abruptly: We note that if H_0 represents the Hamiltonian of our "reference" system, and H the Hamiltonian of a system of interest, a single trajectory of the time-dependent Hamiltonian,

$$H(t)=H_0+C(T)(H-H_0)\,, \tag{2}$$

where $C(t=0)=0$ and $C(t=T=\text{the switching time})=1$, connects surfaces of constant phase volumes and, further, if the time evolution is slow, constant entropies. This allows direct computation of the entropy of the system of interest by computation of a classical trajectory.

These remarks follow from the observation of Hertz in 1910 that the energy shell [whose phase volume Ω gives the semiclassical, or Thomas-Fermi, entropy as $S=k\times\ln(\Omega)$] is an adiabatic invariant for a "slowly"-time-varying Hamiltonian system.[7] Thus, should the change in $C(t)$, above, be slow, a trajectory starting on an energy shell of H_0 ends up on the unique energy shell of H which, via Liouville's theorem, has the identical phase volume. Computation of classical trajectories thus can yield $E(\Omega)$, Ω being the initial phase volume of an energy shell of H_0. Ω is analytically known if H_0 is separable, allowing calculation of $E(\Omega)$ and thus $E(S)$ [or $S(E)$ as $E(S)$ is monotonic] for a strongly interacting system. These relations are summarized in Fig. 1.

We show by direct numerical demonstration that use-

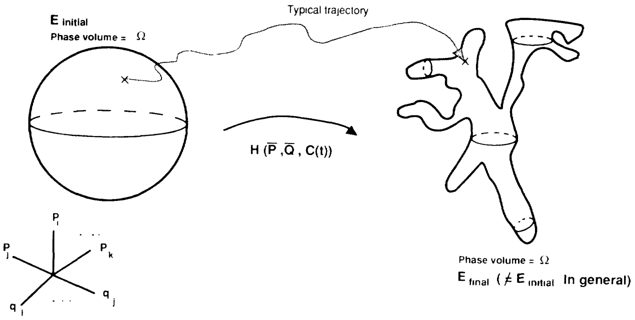

FIG. 1. The Liouville and Hertz invariants. The time-dependent Liouville theorem implies that an initial phase-space surface conserves phase-space volume Ω, independent of switching rate. *If* $C(t)$ *is adiabatic,* then an energy shell of H_0 (at energy E_{initial} and phase volume Ω) is mapped into precisely that energy shell of H (at energy E_{final}) which has the same phase volume Ω. We can thus obtain $E_{\text{final}}(\Omega)$ from a single trajectory of the time-dependent Hamiltonian, as a single trajectory is sufficient to determine E_{final}. Appropriate choice of H_0 implies knowledge of Ω, and thus we have obtained the energy of a strongly interacting system as a function of its phase volume Ω.

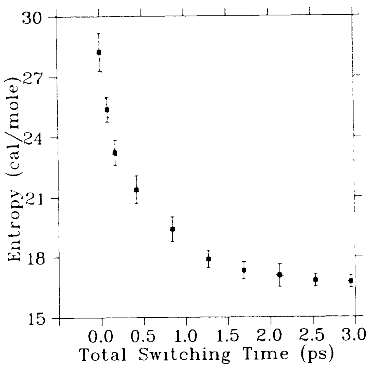

FIG. 2. Entropy of ST2 water model as a function of total switching time with density 1.0 g/cm^3, temperature of 27 °C, and an integration time step of 0.24 fs. Vertical bars indicate the rms deviation of each calculation, based on five independent trajectories for each switching time. The error bars thus indicate the magnitude of statistical errors. Systematic error, due to insufficient switching time, can be seen by the deviation from the converged entropy value, and is independent of statistical error. For example, instantaneous switching shows a very large systematic error (≈ 11 cal/mole) and much smaller statistical error (≈ 2 cal/mole).

ful results may be obtained *both* in the case that H_0 is separable, allowing calculation of *absolute* entropies of strongly interacting systems, and in the case where $H(t)$ is strongly interacting for all $0 < t < T$, allowing calculation of entropy and free-energy *differences*. For one degree of freedom, a bounded trajectory defines the energy shell, and the Hertz invariant is equivalent to conservation of action,[8] the familiar Ehrenfest adiabatic invariant.[9,10] For two degrees of freedom, adiabaticity of the energy shell had been recognized, independently of Hertz, in the plasma physics community, and Ott and co-workers[11] have determined, assuming ergodicity, the asymptotic "goodness" of a "chaotic" invariant (which is that of Hertz) as a function of switching time T, with seemingly discouraging results.

In this Letter, we present evidence for the following: (1) Contrary to the theoretical analysis of Ref. 11, the method appears to be quite efficient. Converged results are obtained in times very short compared to the ergodic time scale, and thus ergodicity is a sufficient, rather than necessary, criterion for the utility of the method, which can succeed even when H_0 is integrable, a perhaps surprising result. (2) Preservation of dynamical adiabaticity suggests the use of *smooth* switching functions, which are indeed found to substantially improve convergence. (3) Extension of the method to include Nosé Hamiltonian dynamics allows direct dynamical computation of free-energy differences.

As an illustration, we consider computation of the entropy of liquid water. The ST2 and TIP4P models familiar from earlier MC and MD studies[12,13] were investigated to obtain absolute entropies and free energies. The intermolecular interactions were truncated smoothly based on the oxygen-oxygen separations.[14] Five independent equilibrium configurations of the same total energy $E_{\rm water}$ were obtained by traditional MD equilibration for the fully interacting system with density 1.0 g/cm^3 and an average temperature of 27 °C. The interaction was then slowly switched off while continuing integration of the classical MD trajectory. The final energy of each classical trajectory is then an estimate of the energy of an ideal gas with identical entropy to the water model. $E(S)$, and thus $S(E)$, are known for the ideal gas. The final energy of each trajectory thus yields an entropy, the average of such entropies being $\bar{S}$. $E_{\rm water}(\bar{S})$, and thus $\bar{S}_{\rm water}(E)$, has then been determined for the water model. Further, sampling and dynamical errors are determined by calculations of $\Delta S_{\rm rms} = \langle S^2 - \bar{S}^2 \rangle^{1/2}$. Figure 2 shows the typical behavior of entropy as a function of total switching time. The excess entropy and excess Helmholtz free energy, defined with respect to an ideal-gas reference state with the same density and temperature, as well as the entropy calculated via the Hertz invariance, are shown in Table I and are in reasonable agreement with previous works[15-17] using the same models.

How do these results depend on the choice of switching function? What does slow mean in practice? Analogous semiclassical quantization by adiabatic switching of invariant tori indicates that the convergence of the final energy is proportional to $T^{-(n+1)}$, where T is the total switching time and n is the number of continuous derivatives of switching function, $C_n(t)$, at $t = 0$ *and* T.[10,18]

TABLE I. Calculation of entropy and Helmholtz free energy of water using the ST2 (Ref. 12) and TIP4P (Ref. 13) models. Comparison is made with results of prior simulations using the same models. ΔS is excess entropy and ΔA is excess Helmholtz free energy at 27 °C with an integration time step of 0.24 fs and a total of 10000 switching steps. Our results are an average over five classical trajectories.

		Present theoretical adiabatic switching calculations				Results of prior simulations	
Type of model	Number of molecules	S (cal/mole K)	A (kcal/mole)	ΔS (cal/mole K)	ΔA (kcal/mole)	ΔS (cal/mole K)	ΔA (kcal/mole)
ST2	80	16.7 ± 0.1	-13.08 ± 0.03	-14.1 ± 0.1	-5.60 ± 0.03	-17.1[a]	-5.4[a]
TIP4P	80	17.7 ± 0.3	-13.27 ± 0.09	-13.1 ± 0.3	-5.79 ± 0.09	-16.0[b]	-5.3[b]
TIP4P	216	17.1 ± 0.1	-13.34 ± 0.03	-13.8 ± 0.1	-5.86 ± 0.03	-13.6 ± 1.1[c]	-5.4 ± 0.3[c]

[a] Reference 16 and has only 64 molecules.

[b] Reference 17.

[c] Reference 15.

The dependence on n for the Hertz method is less strong, but substantial. Six switching functions were defined and studied, Eqs. (3)-(8), below. The functions are expressed in terms of the variable $\tau = t/T$, and defined in the interval $0 \le t \le T$:

$$C_0(t) = \tau\,, \qquad (3)$$

$$C_1(t) = -\tau^2(2\tau - 3)\,, \qquad (4)$$

$$C_2(t) = \tau - \sin(2\pi\tau)/2\pi\,, \qquad (5)$$

$$C_3(t) = -\tau^4(20\tau^3 - 70\tau^2 + 84\tau - 35)\,, \qquad (6)$$

$$C_4(t) = \tau^5(70\tau^4 - 315\tau^3 + 540\tau^2 - 420\tau + 126)\,, \qquad (7)$$

$$C_\infty(t) = \exp\left[-\frac{A}{t}\exp\left[\frac{B}{t-T}\right]\right], \qquad (8)$$

where $B = (T^2/2\ln 2)(1 - T^{-1}\ln 2)$ and $A = \frac{1}{2}T\ln(2) \times \exp(2B/T)$. These functions are extended outside the switching interval by defining $C_n(t) = 0$ for $t \le 0$ and $C_n(t) = 1$ for $t \ge T$. The C_∞ function has essential singularities at $t = 0$ and $t = T$, and has infinite contact. The 216 TIP4P water model at 1.0 g/cm^3 and 27 °C was used in order to compare the effect of these six switching functions, with an integration time step of 0.24 fs. (The C_2 function was used in the calculations of Tables I and II.) Defining an error function,

$$\delta(T) = \ln\{\exp[S(T)/k] - \exp[S(\infty)/k]\}\,,$$

where $S(T)$ is an entropy which is a function of total switching time T and $S(\infty)$ is the asymptotic equilibrium value of entropy, indicates (see Fig. 3) that the switching functions with more than two continuous derivatives have good convergence at $T \ge 2.4$ ps ($\ge 10\,000$ time steps), but the C_0 and C_1 functions give substantially slower convergence. The C_∞ function is not useful for practical computation although presumably its asymptotic convergence rate would be faster than the others. The form of the switching functions thus plays a crucial role in calculating entropy, as befits a dynamical switching method. Nonlinear methods[3] which carry the Hamiltonian, $E = (1 - \tau^m)H_0 + \tau^m H$, are often used. Such a switching function is thus "smooth" near $\tau = 0$, but approaches the asymptote, $\tau = 1$, more sharply than in the linear case, and thus may actually slow convergence of the final results.

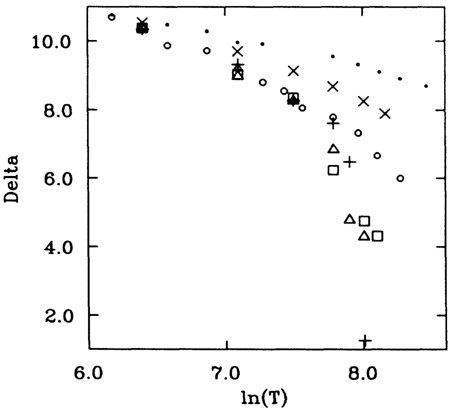

FIG. 3. Error function (defined in the text) vs logarithm of total switching time. Solid circles indicate C_∞ function; crosses, C_0; open circles, C_1; squares, C_2; triangles, C_3; and plusses, C_4. T is in units of fs. The (surprisingly) strong dependence on the choice of switching function suggests a rethinking of the optimal choice of the integration paths in determination of the entropy and various free energies.

The Hertz idea is useful within the context of other ensembles. For example, Nosé introduced a canonical (constant temperature) ensemble MD method[19] with an extended (Nosé) Hamiltonian, shown here for a three-dimensional system:

$$H = H_0(\mathbf{p}/\Phi, \mathbf{q}) + P_\Phi^{(2)}/2Q + (f+1)kT_{\rm eq}\ln\Phi\,. \qquad (9)$$

In Eq. (9) P_Φ is the conjugate momentum of Φ, Q is a parameter of dimension energy × (time)^2 and behaves as a mass for the motion of Φ, $T_{\rm eq}$ is the externally set temperature, and H_0 is the Hamiltonian of the physical system. If $f = 3N$, the microcanonical partition function for the Nosé Hamiltonian H may be written as

$$Z = \frac{1}{3N+1}\left(\frac{2\pi Q}{kT_{\rm eq}}\right)^{1/2}\exp\left(\frac{E}{kT_{\rm eq}}\right)Z_c(T_{\rm eq})\,, \qquad (10)$$

where Z_c is the partition function of the canonical ensemble for the physical system H_0. The usual Hamiltonian MD simulation via Eq. (9) gives canonical averages for the physical subsystem.

Now consider an adiabatic change of H_0, of Eq. (9), to some reference Hamiltonian, $H_0^{\rm ref}$. The microcanonical partition function of the new Nosé Hamiltonian may similarly decompose as

$$Z^{\rm ref} = \frac{1}{3N+1}\left(\frac{2\pi Q}{kT_{\rm eq}}\right)^{1/2}\exp\left(\frac{E'}{kT_{\rm eq}}\right)Z_c^{\rm ref}(T_{\rm eq})\,, \qquad (11)$$

where $Z_c^{\rm ref}$ is the canonical partition function of the reference $H_0^{\rm ref}$.

Now, for an adiabatic transformation $Z^{\rm ref} = Z$, as the total volume of phase space is invariant. Therefore, for an adiabatic change,

$$Z_c(T_{\rm eq}) = \exp\left(\frac{E' - E}{kT_{\rm eq}}\right)Z_c^{\rm ref}(T_{\rm eq})\,. \qquad (12)$$

This relationship can be transformed to more familiar form, $\Delta A = A - A^{\rm ref} = E - E'$. That is, the Helmholtz free-energy difference between two subsystems described by H_0 and $H_0^{\rm ref}$ at the same temperature $T_{\rm eq}$ is equal to the total energy difference of the Nosé Hamiltonian under the adiabatic transformation. Thus the integration of a single microcanonical classical trajectory for the time-dependent Nosé Hamiltonian gives an estimate of a free-energy change in the constant-temperature physical system. This can be thought of as a dynamical derivation of the slow growth method, whose original deriva-

TABLE II. Difference in Helmholtz free energy per particle (in Lennard-Jones unit) between Lennard-Jones fluid and an inverse-twelve soft-sphere fluid on the isotherm $kT/\varepsilon=2.74$. Total of 8000 switching steps.

$N\sigma^3/V$	N	This work ΔA	Previous Monte Carlo results [a]
0.500	108	-5.951 ± 0.004	-5.95 ± 0.01
0.800	108	-11.713 ± 0.005	-11.68 ± 0.01
0.835	108	-12.506 ± 0.005	-12.49 ± 0.015
0.850	108	-12.846 ± 0.005	-12.85 ± 0.015

[a] Reference 20.

tion relied on thermodynamic perturbation theory.[4,5] As a numerical test of this relation, we have investigated the Helmholtz free-energy difference for a Lennard-Jones fluid and an inverse-twelve soft-sphere fluid at the same temperature. This was done at four different densities on the supercritical isotherm $kT/\varepsilon=2.74$. Our calculations are summarized in Table II. Free-energy differences calculated by the Hertz method are in very good agreement with previous work.[20]

In summary, we have presented a dynamical method for computation of the entropy and free energy of dense atomic and molecular fluids and a new derivation of the slow growth method. A dramatic change in convergence as a function of switching function was empirically demonstrated. Several theoretical questions now arise. In an earlier analysis by Ott,[11] the requirement of pointwise convergence of the energy shell required "switching times" long compared to ergodicity time, and gave, even then, very slow $T^{-1/2}$ rates of asymptotic convergence, while rates of order $T^{-1/4}$ or faster are found here, for times of only a few molecular librational periods. The results here show that good "average" results (in the sense that all that we require is that the mean of the final switching energy surface is correct) are obtained in times very small compared to the ergodicity time, and with what is empirically determined to be a rather faster rate of convergence than that of Ott and co-workers.[11] In fact, useful averaged results are obtained where ergodicity fails. The dependence of the rate of convergence of results on the choice of the switching function, as well as the obtaining of converged results for dynamics run on a subergodic time scale, suggests the need for further theoretical analysis of the Hertz method and also of traditional MD, and most certainly the slow growth, approaches to computation of the entropy and free energy, as these may well contain implicit, but previously unrecognized, dynamical components.

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