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Free energy via thermostatted dynamic potential-energy changes

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Three dynamical methods for computing canonical-ensemble Helmholtz free energies are discussed and compared for a thermostatted six-body harmonic chain. We use a Martyna-Klein-Tuckerman thermostat [J. Chem. Phys. **97**, 2635 (1992)] with six time-reversible friction coefficients to study both single-trajectory and ensemble-averaged free-energy changes. Though all three dynamic methods produce identical long-time averages, the one based on Kirkwood's coupling-parameter theory [J. Chem. Phys. **3**, 300 (1935)] converges much more rapidly than do the two based on time-integrated heat transfer.

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I. INTRODUCTION

"New" computational free-energy methods have their conceptual roots in Gibbs's microscopic statistical mechanics and Clausius's macroscopic thermodynamics. Entropy furnishes the link between these classic microscopic and macroscopic approaches. Gibbs's *statistical* entropy is a measure of the accessible phase-space volume $S_{\text{Gibbs}} \equiv k \ln \Omega$, where k is Boltzmann's constant. In the case of Gibbs's microcanonical ensemble, the available phase volume $\Omega(N, E, V)$ is constrained by the total mass, momentum, and energy of the system. Clausius's *thermodynamic* entropy is an integrated measure of the reversible heat taken in, divided by the corresponding ideal-gas-thermometer temperature T . The heat transfers $\{\Delta Q\}$ take place along a reversible path linking a standard zero-entropy state to the state of interest

$$S_{\text{Clausius}} \equiv \int (\dot{Q}/T) dt .$$

It was Gibbs's remarkable finding that the microscopic state-counting and macroscopic heat-transfer methods of determining the equilibrium entropy agree, $S_{\text{Gibbs}} \equiv S_{\text{Clausius}}$.

Once fast computers became available, numerical methods for determining entropy were developed, based on these same two definitions [1]. Both microscopic statistical state counting and macroscopic thermodynamic integration have been used to determine the entropy S . A third computational approach has been developed more recently and is unique to computation. The basis of this new dynamical approach is the adiabatic principle of

mechanics. This principle asserts that whenever external work is performed sufficiently slowly ("reversibly"), the system occupies near-enough-to-equilibrium states that the entropy is a constant of the motion. When state changes occur at finite rates, the deviations from equilibrium are typically *quadratic* in the rates. The dissipation provided by viscosity and heat conduction, as well as the *thermodynamic* dissipation we quantify in this paper, are examples. The phenomenological nonequilibrium coefficients describing these close-to-equilibrium state changes are accessible through equilibrium linear-response ("Green-Kubo") theory.

Changes in system energy need not be induced by mechanical work or by heating. In Section 2 we recall Kirkwood's idea for determining free energy by varying the Hamiltonian. We then detail Watanabe and Reinhardt's suggestion that this idea be applied dynamically. A dynamics appropriate to Hamiltonian variation is described in Sec. III. It is the Martyna-Klein-Tuckerman generalization of Nosé's isothermal molecular dynamics. With the isothermal dynamics of Martyna, Klein, and Tuckerman, computation of Watanabe and Reinhardt's extension of Kirkwood's free-energy idea can be carried out. We extend this approach in Sec. IV. There we derive results linking free-energy changes to time-averaged values of isothermal friction coefficients. Section V describes a particular simple one-dimensional chain model, with a known free energy, to which we apply all these ideas. Our numerical results, including an evaluation of the complete spectrum of Lyapunov exponents for this system, and our conclusions, make up Secs. VI and VII.

II. STATIC AND DYNAMIC COUPLING-PARAMETER METHODS

In the usual situation, thermodynamic *work* is performed by manipulating some of the system coordinates $\{q\}$. Work can involve a volume change or a shape change, as well as motion within an external field. *Heat* is transferred to a system differently, by varying some of the system momenta $\{p\}$ at fixed coordinate values.

External work need not affect the particle coordinates by prescribing their time variation as in a volume, shape, or field change. Instead, the *functional dependence* of the forces $\{F(\{q\})\}$ on the particle coordinates $\{q\}$ can be gradually changed. In this way, one thermodynamic material can be transformed into another. The simplest way to realize this computational alchemy is to let the potential function $\Phi(\{q\})$ vary with time. Likewise, and equivalently, the Hamiltonian $H \equiv \Phi(\{q\}) + K(\{p\})$ varies with time. The conventional description of such a change of forces, potential energy, and Hamiltonian uses a coupling parameter λ which varies from 0 to 1. If we specify a *time dependence* for the coupling parameter, $\lambda(t')$, with a dummy time variable t' , we can likewise regard the Hamiltonian as changing from H_0 , at time 0, to $H_t \equiv H_1$ at time t :

$$H(\lambda) \equiv H(t') \equiv (1-\lambda)H_0 + \lambda H_1 \equiv (1-\lambda)H_0 + \lambda H_t, \quad (2.1)$$

$$\Phi(\lambda) \equiv \Phi(t') \equiv (1-\lambda)\Phi_0 + \lambda\Phi_1 \equiv (1-\lambda)\Phi_0 + \lambda\Phi_t. \quad (2.2)$$

It is worth emphasizing that H_0 , H_1 , Φ_0 , and Φ_1 are not themselves functions of λ . $\lambda(t')$ furnishes a linear interpolation linking the two material end points. In simulating a thermodynamically *reversible* process, the coupling parameter $\lambda = \lambda(t')$, which transforms the Hamiltonian from H_0 at time 0 to H_t at time t , must vary sufficiently slowly and smoothly between its initial and final values, 0 and 1.

The idea of such a varying Hamiltonian was used in statistical mechanics by Kirkwood [2], but in the restricted context of equilibrium ensemble theory, without an explicit time dependence for λ . Watanabe and Reinhardt [3] extended Kirkwood's idea by varying λ dynamically, with time. Either Kirkwood's original approach, or Watanabe and Reinhardt's dynamic generalization of it, can, for instance, be used to add a perturbing attractive potential to a repulsive reference potential, or to add the full interaction potential to an ideal gas.

The nonequilibrium dynamics of an ensemble of trajectories, with differing initial conditions, and subject to isothermal boundary conditions—contact with a thermal reservoir at temperature T via thermostated equations of motion—can be cast in the familiar framework of hydrodynamics: The time-dependent density of trajectories in phase space is the distribution function $\rho(\mathbf{x}, t)$, where the phase-space position $\mathbf{x} \equiv (\{q\}, \{p\}, \{\xi\})$ is the collection of N -particle, d -dimensional coordinates and momenta, as well as M thermostating control variables $\{\xi\}$, described in more detail later. The normalization of ρ , the ensemble average of the energy E , and the entropy S are given by

$$\begin{aligned} 1 &\equiv \int d\mathbf{x} \rho(\mathbf{x}, t), \\ E(t) &\equiv \int d\mathbf{x} \rho(\mathbf{x}, t) H(\mathbf{x}) \equiv \langle H(t) \rangle, \\ S(t) &\equiv -k \int d\mathbf{x} \rho(\mathbf{x}, t) \ln \rho(\mathbf{x}, t) \equiv -k \langle \ln \rho(t) \rangle. \end{aligned} \quad (2.3)$$

The internal energy function $H(\mathbf{x})$ is defined by

$$H(\mathbf{x}) = K(\{p\}) + \Phi(\{q\}) + H_\xi(\{\xi\}),$$

where K and Φ are the kinetic and potential energies of the particles and H_ξ is the contribution of the thermostats.

Because the trajectories are independent of one another, the $(2dN + M)$ -dimensional ensemble “fluid” is characterized by a local fluid velocity $\mathbf{u}(\mathbf{x}, t) = \dot{\mathbf{x}}(\mathbf{x}, t)$, which we recognize as the many-body equation of motion. This simple dependence of \mathbf{u} on position is quite different from the fluid velocity to which we are accustomed in hydrodynamics, where mass elements transfer momentum and energy to one another. Because of this simplicity (at the expense of a large number of degrees of freedom, of course), the dynamics of an ensemble of trajectories in nonequilibrium statistical mechanics requires only Liouville's continuity equation for ρ :

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) &\equiv 0 = \left[\frac{\partial \rho}{\partial t} + \mathbf{u} \cdot \nabla \rho \right] + \rho \nabla \cdot \mathbf{u} \\ &= \frac{d\rho}{dt} + \rho \dot{\epsilon} \end{aligned} \quad (2.4)$$

$$\implies \dot{\epsilon} \equiv \nabla \cdot \mathbf{u} \equiv \frac{-d \ln \rho}{dt}, \quad (2.5)$$

where the last expression is the local rate of expansion of an infinitesimal phase-space volume element. The rate of change of the entropy of the ensemble is therefore given by the relation

$$\dot{S} = -k \left\langle \frac{d \ln \rho}{dt} \right\rangle = k \langle \dot{\epsilon} \rangle. \quad (2.6)$$

For the microcanonical (constant-energy) ensemble where there is no coupling of the particles to a heat reservoir, so that the equations of motion are Newtonian (Hamiltonian),

$$\mathbf{u}(\mathbf{x}, t) = \dot{\mathbf{x}}(\mathbf{x}, t) = \{ \dot{q} = p/m; \dot{p} = F(q) = -\nabla \Phi \}, \quad (2.7)$$

the local rate of phase-space volume expansion is identically zero:

$$\dot{\epsilon} = \nabla \cdot \mathbf{u} = \sum \left[\frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} \right] \equiv 0. \quad (2.8)$$

Thus, for an ensemble of isolated adiabatic systems governed by Newtonian mechanics, the entropy is a constant: $\dot{S} = k \langle \dot{\epsilon} \rangle = 0$. For an *ensemble* of thermostated systems, however, S is not constant—when work is done on an isothermal system, the heat extracted by the thermal reservoirs is directly related to the contraction of the available phase space relative to equilibrium. Therefore, we see, qualitatively at least, how the Helmholtz free energy $A \equiv E - TS$ must be a minimum at equilibrium.

As usual, in all of our equations the $\{q\}$ are generalized coordinates and the $\{p\}$ are the corresponding conjugate momenta. Watanabe and Reinhardt [3], following the example of Torrie and Valleau [4], made use of the adiabatic principle to correlate the free energy for a simple inverse-12th-power soft-sphere Hamiltonian H_0 with that of a more complicated Lennard-Jones system, including inverse-6th-power attraction H_1 , with unbelievable success. See Table II of Ref. [3], but, in the case of the first two entries, note the discrepancy between the number of particles (108) in that Table and the number of particles (32) actually cited in the original Ref. [4].

Relatively recently, but inspired by Gibbs's vintage-1900 ensembles, extensions of straightforward isoenergetic Newtonian computer simulation to new isothermal and isobaric forms have developed [5–9]. Reference [9] presents a useful overview of these approaches, beginning with Nosé's seminal 1984 paper. With the new deterministic time-reversible methods in hand, it is natural to study the analogs of the adiabatic principle for slowly changing dynamical systems connected to thermal and mechanical reservoirs. Isothermal dynamics, for instance, corresponds to a system connected to a constant-temperature heat bath, so that the reversible isothermal thermodynamic work corresponds to an isothermal change in the corresponding *free* energy, including heat transfer, rather than to an adiabatic change of internal energy. We undertake here an exploration of this natural extension of the work of Kirkwood, Watanabe, and Reinhardt, applying a particularly simple and robust computational scheme [9] to a simple model Hamiltonian for which analytic free energies are known.

III. ISOTHERMAL EQUATIONS OF MOTION

Here we focus on isothermal isochoric dynamics, corresponding to Gibbs's canonical ensemble. The corresponding free energy is the Helmholtz free energy $A(N, V, T)$ for a system of N particles in d space dimensions, with dN degrees of freedom, confined to a volume V , and at a temperature T . The corresponding equations of motion must be consistent with the canonical phase-space distribution. In the simplest ["Nosé-Hoover"] case, the equations incorporate a *single* friction coefficient ξ or z , which responds to fluctuations of the kinetic energy about its mean value $K_0 = 3NkT/2$ in three space dimensions ($d=3$) or $K_0 = NkT/2$ in one dimension ($d=1$). The equations of motion can be written in either of two equivalent forms:

$$\left\{ \frac{dq}{dt} = p/m; \frac{dp}{dt} = -\nabla\Phi - \xi p \right\}_n, \quad n=1, 2, \dots, dN, \quad (3.1)$$

$$\frac{d\xi}{dt} = [(K/K_0) - 1]/\tau^2$$

or

$$\left\{ \frac{dq}{dt} = p/m; \frac{dp}{dt} = -\nabla\Phi - \nu zp \right\}_n, \quad n=1, 2, \dots, dN, \quad (3.2)$$

$$\frac{dz}{dt} = \nu[(K/K_0) - 1].$$

We use n as a subscript for the dN similar equations of

motion for the $\{q\}$ and $\{p\}$. The two possibilities for defining the friction coefficient are simply related: $\xi \equiv \nu z \equiv z/\tau$. Note that ξ , ν , and $1/\tau$ have units of frequency, while z is dimensionless. The phase-space continuity equations for the densities $\rho(\{q\}, \{p\}, \{\xi\})$ and $\rho(\{q\}, \{p\}, \{z\})$ show that the corresponding canonical distributions are stationary:

$$\rho_{\text{Gibbs}} \propto \exp[-H(q, p)/kT] \exp[-dN\xi^2\tau^2/2] \\ \propto \exp[-H(q, p)/kT] \exp[-dNz^2/2].$$

The Gaussian friction-coefficient distribution shows that the friction coefficient, ξ or z , takes on values of order $N^{-1/2}$, so that the frictional-force contribution to the dynamics of the n th degree of freedom, $-\xi p_n = -\nu zp_n$, vanishes, in the thermodynamic limit, in the same way as do the fluctuations in intensive thermodynamics variables.

This single-friction-coefficient representation is adequate for treating some systems—those with strong enough mixing characteristics for a thorough exploration of phase space. Such thorough mixing appears to be present in the usual three-dimensional fluid and solid systems simulated with molecular dynamics [10]. But the single-friction-coefficient dynamics *fails* to give the complete canonical distribution for sufficiently *nonmixing* systems, such as a free particle or a one-dimensional harmonic oscillator. Such systems explore only a part of their phase spaces, with that part depending upon the initial conditions. Many ideas have been advanced to provide better mixing through more complicated versions of deterministic friction [7–9].

In the present work we adopt an elegant generalization of the single-friction-coefficient idea to chains of M interacting friction coefficients, which Martyna, Klein, and Tuckerman introduced [9]. They showed that this approach can be sufficiently mixing to generate a canonical distribution for a single harmonic oscillator. As a starting point, we choose Eq. (10) of Ref. [9] to be the basis for our discussion of canonical-ensemble dynamics. For simplicity we specialize that equation to the case of four thermostat variables $\{\xi_1, \xi_2, \xi_3, \xi_4\}$ governed by four parameters with the same physical units [mass \times length²] as a moment of inertia (unfortunately called "masses" by most workers) $\{Q_1, Q_2, Q_3, Q_4\}$ from which the general case, with M thermostat variables and M parameters, should be clear:

$$\left\{ \frac{dq}{dt} = p/m; \frac{dp}{dt} = F - \xi_1 p \right\}_n, \quad n=1, 2, \dots, dN \\ \frac{d\xi_1}{dt} = [2K - 2K_0]/Q_1 - \xi_2 \xi_1, \\ \frac{d\xi_2}{dt} = (Q_1 \xi_1^2 - kT)/Q_2 - \xi_3 \xi_2, \\ \frac{d\xi_3}{dt} = (Q_2 \xi_2^2 - kT)/Q_3 - \xi_4 \xi_3, \\ \frac{d\xi_4}{dt} = (Q_3 \xi_3^2 - kT)/Q_4, \\ 2K \equiv \sum p^2/m; \quad 2K_0 \equiv dN kT. \quad (3.3)$$

Martyna, Klein, and Tuckerman observed that the thermal feedback associated with the thermostat variables $\{\xi(Q)\}$ is most efficient if their fluctuation times correspond to a typical collision time τ or, equivalently, to a typical vibrational frequency ν , of the thermodynamic system described by the dN coordinate-momentum pairs $\{q, p\}$. Thus a reasonable choice for the parameter Q_1 is given by

$$Q_1 = dN kT / \nu^2 \equiv dN kT \tau^2,$$

assuring fluctuations of order $N^{-1/2}$ in ξ_1 . The remaining $M-1$ thermostat parameters $\{Q_2, Q_3, \dots, Q_M\}$ are not directly linked to the thermodynamic system at all. Their purpose is to provide fluctuations in the primary control variable ξ_1 , through its chain of interactions with $\xi_2, \xi_3, \dots, \xi_M$. Thus the remaining Q 's can be set equal to $Q_{i>1} = kT / \nu^2 \equiv kT \tau^2$, so as to induce fluctuations of order $\nu \equiv 1/\tau$ in the friction coefficients $\{\xi_{i>1}\}$. Then the complete set of thermostated equations becomes

$$\left\{ \frac{dq}{dt} = p/m; \frac{dp}{dt} = F - \xi_1 p \right\}_n, \quad n = 1, 2, \dots, dN$$

$$\frac{d\xi_1}{dt} = [(K/K_0) - 1] / \tau^2 - \xi_2 \xi_1,$$

$$\frac{d\xi_2}{dt} = [dN \xi_1^2 - (1/\tau^2)] - \xi_3 \xi_2, \quad (3.4)$$

$$\frac{d\xi_3}{dt} = [\xi_2^2 - (1/\tau^2)] - \xi_4 \xi_3,$$

$$\frac{d\xi_4}{dt} = [\xi_3^2 - (1/\tau^2)].$$

In this formulation it is plain to see that the friction coefficients have units of inverse time. It is easy to verify, by direct substitution, that these equations of motion are consistent with the stationary equilibrium canonical distribution in the "extended" phase spaces, that is, phase spaces including the M friction coefficients $\{\xi\}$ as additional coordinates:

$$\rho_{\text{Gibbs}} \propto \exp[-H(q, p)/kT] \exp\left[-\sum_{i=1}^M Q_i \xi_i^2 / 2kT\right],$$

$$\rho_{\text{Gibbs}} \propto \exp[-H(q, p)/kT]$$

$$\times \exp\left[-\left[dN \tau_1^2 \xi_1^2 + \sum_{i=2}^M \tau_i^2 \xi_i^2\right] / 2\right].$$

An alternative, more transparent, way of rewriting the Martyna, Klein, and Tuckerman system of equations (1) is to introduce *dimensionless* "friction coefficients" $\{z\}$ with associated frequencies $\{\nu\}$, so that $\xi_i \equiv \nu_i z_i$. With the parameter choices

$$Q_1 = dN kT / \nu_1^2, \quad Q_2 = kT / \nu_2^2,$$

$$Q_3 = kT / \nu_3^2; \dots, \quad Q_M = kT / \nu_M^2, \quad (3.5)$$

the Martyna, Klein, and Tuckerman equations give the following system:

$$\left\{ \frac{dq}{dt} = p/m; \frac{dp}{dt} = F - \nu_1 z_1 p \right\}_n, \quad n = 1, 2, \dots, dN.$$

$$\frac{dz_1}{dt} = \nu_1 [(K/K_0) - 1] - \nu_2 z_2 z_1,$$

$$\frac{dz_2}{dt} = \nu_2 (dN z_1^2 - 1) - \nu_3 z_3 z_2,$$

$$\frac{dz_3}{dt} = \nu_3 (z_2^2 - 1) - \nu_4 z_4 z_3,$$

$$\frac{dz_4}{dt} = \nu_4 (z_3^2 - 1),$$

$$2K \equiv \sum_n p^2 / m, \quad 2K_0 \equiv dN kT.$$

$$(3.6)$$

The inverse-square-root dependence $z_1 \propto N^{-1/2}$, with dN thermostated degrees of freedom, is perhaps clearest from (3.4) or (3.6). The choice among the three formulations, (3.3), (3.4), or (3.6), is purely aesthetic. *Any* one of the three formulations generates a time-reversible deterministic dynamics, robust and consistent with Gibbs's canonical phase-space distribution. In terms of the dimensionless friction coefficients, the distribution has the form

$$\rho_{\text{Gibbs}} \propto \exp[-H(q, p)/kT]$$

$$\times \exp\left[-\left[dN z_1^2 + \sum_{i=2}^M z_i^2\right] / 2\right].$$

IV. COMBINING KIRKWOOD'S APPROACH WITH ISOTHERMAL MOLECULAR DYNAMICS

When the underlying Hamiltonian is varied, reversibly, under isothermal conditions, the quasistatic change in Helmholtz free energy can be written as an integral, over the thermodynamic path, of the time-averaged total perturbation energy $(\Phi_t - \Phi_0)$:

$$A_t - A_0 \equiv \int_0^t \langle (H_t - H_0) \rangle_\lambda \frac{d\lambda}{dt'} dt'$$

$$\equiv \int_0^t \langle (\Phi_t - \Phi_0) \rangle_\lambda \frac{d\lambda}{dt'} dt'. \quad (4.1)$$

It should be emphasized that $H_t - H_0$ and $\Phi_t - \Phi_0$ are not functions of the coupling parameter λ . The dynamics governing the motion, through $H[\lambda(t')]$, *does* depend on the coupling, so that the averages carried out at time t' , $\langle \rangle_\lambda$, reflect the underlying value of the coupling parameter $\lambda(t')$.

Kirkwood's coupling-parameter version of this relation,

$$\Delta A \equiv \int_0^1 \langle (H_1 - H_0) \rangle_\lambda d\lambda, \quad (4.2)$$

is a familiar consequence of Gibbs's equilibrium statistical mechanics. The time-dependent forms follow provided that the motion is quasiergodic, so that the dynamical average at time t' corresponds to Gibbs's phase average

computed with the coupling parameter $\lambda(t')$. The Kirkwood relation in turn follows from the definition of a *coupling-parameter-dependent* canonical partition function $Z(\lambda)$, related in the usual way to a coupling-parameter-dependent Helmholtz free energy $A(\lambda)$:

$$\begin{aligned} Z(N, V, T, \lambda) &\equiv \sum \exp[-H(\lambda)/kT] \\ &\equiv \exp[-A(N, V, T, \lambda)/kT], \\ H(\lambda) &\equiv H_0 + \lambda(H_1 - H_0) \equiv H_0 + \lambda(\Phi_1 - \Phi_0). \end{aligned}$$

The ideal-gas-thermometer temperature T , in a classical dynamical simulation, is defined in terms of the mean kinetic energy per Cartesian degree of freedom: $kT \equiv \langle p^2/m \rangle$. This definition is consistent with the collisional mechanics of a thermometer [11], even in non-equilibrium situations, where Gibbs's entropy is undefined [12]. By separating the Hamiltonian into a coordinate-dependent potential energy $\Phi(q)$ and a momentum-dependent kinetic energy $K(p)$, the free-energy difference $A_1 - A_0$ can more simply be expressed as a potential-energy integral over the coupling parameter λ :

$$A_1 - A_0 \equiv \int_0^1 \langle (\Phi_1 - \Phi_0) \rangle_\lambda d\lambda. \quad (4.3)$$

This statistical technique has been used to study the free-energy difference between solids, liquids, and gases, as well as the free energy of defects which can be introduced by coupling [1]. The quasistatic ensemble formulation becomes equivalent to a dynamical one when λ is given a specified, and sufficiently slow, time dependence $\lambda = \lambda(t)$. Then the integral over λ is equivalent to a *time* integral, with $d\lambda$ replaced by $(d\lambda/dt)dt = \dot{\lambda} dt$:

$$A_t - A_0 \equiv \int_0^t \langle (\Phi_t - \Phi_0) \rangle_\lambda \frac{d\lambda}{dt'} dt'. \quad (4.4)$$

The dynamics at the time t' depends upon the Hamiltonian $H(t')$ through the coupling parameter λ . We wish to explore this dynamical method for Helmholtz free-energy determination here, for a simple and well-understood few-body problem with an analytically known free energy.

The equations of motion, including the friction coefficients $\{\zeta_i\}$ or $\{z_i\}$, with $i = 1, 2, \dots, M$, can be used to derive two alternative expressions for free energy based on heat transfer. From the microscopic standpoint, transferred heat corresponds to an energy change made with fixed coordinates $\{q\}$. Because the friction coefficients $\{\zeta\}_M$ or $\{z\}_M$ transfer heat to the thermodynamic system described by $\{q, p\}_{dN}$, thermodynamics establishes that, for a process sufficiently slow that the quadratic dissipative contributions can be ignored, entropy changes can be expressed in terms of the time-integrated friction coefficients.

To show this, we recall that the phase-space density $\rho(\{\mathbf{x}\})$ now also contains M friction coefficients ζ_i among its variables: $\{\mathbf{x}\} = \{q_n, p_n, \zeta_i\}$, $n = 1, \dots, dN$, $i = 1, \dots, M$. If the Liouville continuity equation (2.4) is used for evaluating (2.6), one finds after insertion of the thermostatted equations of motion (3.3) or (3.4):

$$\dot{S}/k = \left\langle \sum \frac{\partial \dot{\mathbf{x}}}{\partial \mathbf{x}} \right\rangle_\lambda = - \langle dN \zeta_1 + \zeta_2 + \dots + \zeta_M \rangle_\lambda \equiv - \Sigma_\zeta. \quad (4.5)$$

Hence, the isothermal entropy change is given by

$$\begin{aligned} \Delta S/k &= \int (\dot{Q}/kT) dt = \int (\dot{S}/k) dt \\ &= - \int \langle dN \zeta_1 + \sum_{i>1} \zeta_i \rangle_\lambda dt \\ &= - \int \Sigma_\zeta dt, \end{aligned} \quad (4.6)$$

which is the desired result. The notation $\langle \rangle_\lambda$ reminds us that the average of the friction-coefficient sum is affected by the parameter λ , which is switched from 0 to 1 in the time interval under consideration.

The isothermal entropy change may also be expressed in terms of the heat added to the system through the action of the reversible friction coefficient ζ_1 :

$$\Delta S/k = - \left\langle \int \zeta_1 \sum_{n=1}^{dN} (p_n^2/mkT) dt \right\rangle_\lambda, \quad (4.7)$$

where the sum is over all dN system degrees of freedom. The two expressions (4.6) and (4.7) are equivalent. This follows from a computation of the time average

$$\left\langle (d/dt)^{\frac{1}{2}} \left[dN \zeta_1^2 + \sum_{i>1} \zeta_i^2 \right] \right\rangle_\lambda.$$

For simplicity, we derive this relationship in the special case that all the characteristic frequencies are equal, $\{v_i = v = 1/\tau\}$, $i = 1, \dots, M$. Thus, from (3.4) we find

$$\begin{aligned} 0 &\equiv \left\langle \frac{d}{dt} \left(\frac{1}{2} \left[dN \zeta_1^2 + \sum_{i>1} \zeta_i^2 \right] \right) \right\rangle_\lambda \\ &= \left\langle dN \zeta_1 \frac{d\zeta_1}{dt} + \sum_{i>1} \zeta_i \left[\frac{d\zeta_i}{dt} \right] \right\rangle_\lambda \\ &= \left\langle \sum_n \zeta_1 (p^2/mkT) v^2 \right\rangle_\lambda \\ &\quad + [- \langle dN \zeta_1 \rangle_\lambda - \langle \zeta_2 \rangle_\lambda - \langle \zeta_3 \rangle_\lambda - \dots - \langle \zeta_M \rangle_\lambda] v^2, \end{aligned}$$

where all the terms that are cubic in the friction coefficients cancel. This establishes (4.7). As a consequence, the free-energy change can be written in either of two (new) ways:

$$\begin{aligned} A_t - A_0 &\equiv \Phi_t - \Phi_0 + \int_0^t \left\langle \sum_n \zeta_1 p^2/m \right\rangle_\lambda dt' \\ &= \Phi_t - \Phi_0 + kT \int \Sigma_\zeta dt'. \end{aligned} \quad (4.8)$$

The same derivation can be carried out using the dimensionless friction coefficients $\{z\}_M$. That approach gives an equivalent result:

$$\begin{aligned} A_t - A_0 &\equiv \Phi_t - \Phi_0 + \int_0^t \left\langle \sum_n z_1 v_1 p^2/m \right\rangle_\lambda dt' \\ &= \Phi_t - \Phi_0 + kT \int \Sigma_{vz} dt', \end{aligned} \quad (4.9)$$

where Σ_{vz} indicates the time-averaged friction-coefficient sum, with z_1 occurring dN times, and with each friction

coefficient z_i multiplied by its characteristic frequency ν_i .

The analog of Liouville's theorem, for this dynamics in which phase volume is not conserved, relates the time average of the friction-coefficient sum to the sum of *all* the Lyapunov exponents $\{\lambda_\alpha\}$ for which we use the special symbol Λ :

$$\Sigma'_\xi = - \sum_\alpha \lambda_\alpha \equiv -\Lambda \equiv \left\langle \frac{d \ln \rho}{dt} \right\rangle_{\text{ensemble}}.$$

We use a prime in this equation to indicate a long-time average, over many periodic full cycles of the switching parameter, rather than the one-way average, from 0 to 1, indicated by the symbol Σ_ξ , without the prime. The Lyapunov exponents, one for each independent direction in the phase space (including the friction coefficients and the time), have been designated λ_α to avoid confusion with the Kirkwood coupling parameter λ .

In Sec. V we introduce a simple harmonic-chain model, for which the entropy and free energy can be calculated analytically. In Sec. VI we apply both these entropy methods, one based on time averaging the coupling-dependent heat transfer $\xi_1 \sum (p^2/m)$ and the other based on integrating $kT \Sigma_\xi$. We compare these results with the Kirkwood, Watanabe, and Reinhardt free-energy calculation in the chain example described in Sec. V. We also characterize the Lyapunov spectra for this simple model system.

V. HARMONIC-CHAIN MODEL

Our simple one-dimensional ($d=1$) chain model links each of N atoms, with mass m , to its two nearest neighbors with Hooke's-law springs of force constant κ . We impose cyclic (periodic) boundary conditions, so that atoms 1 and N are nearest neighbors, and keep the system center of mass, as well as the momentum associated with the center of mass, fixed. The canonical partition function for this system is a product of $(N-1)$ normal-mode partition functions with a coordinate probability density depending on the potential energy $\Phi(\{q\})$:

$$P(\{q\}) \propto \exp[-\Phi(\{q\})/kT].$$

The temperature T can be maintained in the chain by using a variety of reversible thermostats. The simplest of these is the Gaussian thermostat, which keeps the kinetic energy constant. The Nosé-Hoover thermostat introduces a single additional thermostating variable. Our trials with both these thermostats strongly suggested, but certainly did not prove, a lack of ergodicity. We therefore explored the relatively simple and elegant extension of these thermostats discovered (or invented) by Martyna, Klein, and Tuckerman [9]. These authors showed that their equations of motion are consistent with an extended Gibbsian canonical distribution. They also critically discuss several alternative approaches to isothermal dynamics.

Martyna, Klein, and Tuckerman judged that ergodicity was most efficiently promoted, for an oscillator system, by using at least three thermostating variables. For simplicity we have applied the following version of their equations of motion to a six-atom chain, arbitrarily also

using, just for the sake of symmetry, six thermostating variables $\{\xi_1, \xi_2, \xi_3, \xi_4, \xi_5, \xi_6\}$:

$$\left\{ \begin{aligned} \frac{dq}{dt} &\equiv (p/m); \quad \frac{dp}{dt} \equiv F(q) - \xi_1 p \end{aligned} \right\}_n, \quad n = 1, \dots, 6$$

$$\begin{aligned} \frac{d\xi_1}{dt} &= [\sum (p^2/mkT) - 6]/\tau^2 - \xi_2 \xi_1, \\ \frac{d\xi_2}{dt} &= \xi_1^2 - (1/\tau)^2 - \xi_2 \xi_3, \\ \frac{d\xi_3}{dt} &= \xi_2^2 - (1/\tau)^2 - \xi_3 \xi_4, \\ \frac{d\xi_4}{dt} &= \xi_3^2 - (1/\tau)^2 - \xi_4 \xi_5, \\ \frac{d\xi_5}{dt} &= \xi_4^2 - (1/\tau)^2 - \xi_5 \xi_6, \\ \frac{d\xi_6}{dt} &= \xi_5^2 (1/\tau)^2. \end{aligned} \quad (5.1)$$

We have made the simplest choice for the relaxation time τ , $\tau \equiv 1$, in all of our simulations. We have likewise chosen all of the Q 's equal to $kT\tau^2$. Note that in the dimensionless thermostating version, $\nu_1 = 6^{1/2}$, $\nu_2 = \dots = \nu_6 = 1$. As a supplement, we have also occasionally calculated and included a small (of order 10^{-12}) correction to the coordinates and momenta to prevent drift in the center of mass. Here, the center-of-mass correction is only aesthetic. Such a correction turned out to be *absolutely necessary* in a related nonequilibrium problem involving the transfer of heat between the thermostated "cold" and "hot" ends of few-particle harmonic chains. In that nonequilibrium simulation [13], roundoff errors in the cold and hot centers of mass could be amplified catastrophically by Lyapunov instability.

A simple extension of the conventional Liouville's theorem [9] (2.4) establishes that the stationary Gibbsian probability density for these equations of motion, $\rho(\{q, p, \xi\})$, has the form

$$\rho \propto \exp[-(\Phi/kT) - (K/kT) - (\tau^2/2)(\xi_1^2 + \xi_2^2 + \xi_3^2 + \xi_4^2 + \xi_5^2 + \xi_6^2)].$$

Martyna, Klein, and Tuckerman's results make it plausible that this dynamics is quasiergodic and chaotic, *even for a single harmonic oscillator*. The results we find here, for cyclic chains of six coupled harmonic oscillators, support that view. We also find that statistical averages obtained by following a single dynamical system agree with those obtained by integrating instead over an equilibrium ensemble of initial conditions.

The "chain" of thermostat variables $\{\xi\}$ controls the external heat flow in such a way as to stabilize the kinetic energy. Energy is fed into and extracted from the system $\{q, p\}_6$ by the variable ξ_1 . To test the coupling-parameter free-energy formulation, we have changed the force constant κ describing the six mechanical interactions smoothly from 1 to 4. This results in a doubling of all the chain frequencies and should therefore correspond to an equilibrium increase in Helmholtz free energy of

$NkT \ln 2 = 6kT \ln 2$. It is feasible to accumulate statistics by carrying out thousands of cycles of increase and decrease of κ . For convenience we have chosen $m = 1$, $k = 1$, and $T = 1$ in all of our numerical work, where k is Boltzmann's constant. The ideal-gas-temperature scale establishes that the time-averaged squared momenta and squared thermostat variables should all likewise be equal to unity:

$$\langle p_n^2 \rangle = \langle \zeta_i^2 \rangle \equiv 1 .$$

The Lyapunov exponents associated with a chaotic trajectory describe its sensitivity to perturbations in initial conditions. For the model system here the motion takes place in a 19-dimensional phase space (six coordinates, six momenta, six friction coefficients, and the time). The additional time dimension must be introduced because the equations of motion vary, periodically, with time.

We have solved the linearized motion equations, with the linearized solution vectors necessary to evaluate the complete spectrum [14]. The solution vectors were kept orthonormal by applying Gram-Schmidt orthonormalization after every few time steps.

Because there can be no exponential growth of perturbations in the direction of trajectory propagation and because both the sums $\sum q$ and $\sum p$ are fixed, we would expect to find at least three vanishing Lyapunov exponents for our model.

VI. RESULTS

We have studied three simple alternative representations of the rate-dependent time variation, between 1 and 4, of the force constant κ_{linear} , κ_{cosine} , and $\kappa_{\text{quadratic}}$. These are given by the following relations:

TABLE I. Free-energy changes $\Delta A_{\text{switch}}^{\pm}$ for a cyclic six-atom Martyna-Klein-Tuckerman-thermostatted chain for which the oscillator force constant varies periodically between 1 and 4 at a rate r , as described by (6.1) of the text. The total run time is t and the fourth-order Runge-Kutta time step is 0.005 or 0.01. Linear, cosine, and quadratic force-constant switching data are included in the table. The three different free-energy estimates (all of which agree at zero rate), indicated by $\langle \zeta_i \sum p^2 \rangle_{\lambda}$, $\langle \Delta \Phi \rangle_{\lambda}$, and $\Sigma_{\zeta} \equiv \langle 6\zeta_1 + \zeta_2 + \zeta_3 + \zeta_4 + \zeta_5 + \zeta_6 \rangle_{\lambda}$, are, respectively, based on heat transfer, Kirkwood's coupling parameter, and Liouville's theorem. Λ is the sum of all the Lyapunov exponents. The exact analytic equilibrium free-energy change is $\Delta A \equiv 6kT \ln 2 = 4.159$. The data show that Kirkwood's $\Delta \Phi$ approach is best and that the individual estimates can be either too high or too low, depending upon both the method and the rate. The time integrals of the Lyapunov-exponent sum and the friction-coefficient sums are given for integrals over a cycle. Thus, for the data in the fourth row, the average value of Σ_{ζ} is 0.000 13, and the time integral, over a complete cycle of time $2/0.01 = 200$, is $200 \times 0.000 13 = 0.026$, approximately equal to the difference $4.082 - 4.058 = 0.024$.

Rate r	$10^{-6}t$	$\Delta A_{\text{switch}}^{\pm}$				
		$\int \langle \zeta_i \sum p^2 / m \rangle_{\lambda} dt$	$\int \langle \Delta \Phi \rangle_{\lambda} dt$	$\int \Sigma_{\zeta} dt$	Λ	Σ'_{ζ}
Linear						
0.001	0.90	4.452–4.433	4.163–4.153	4.493–4.477	–0.000 01	+0.000 01
0.002	0.82	4.265–4.254	4.163–4.154	4.311–4.300	–0.000 01	+0.000 01
0.005	0.82	4.021–4.000	4.159–4.138	4.097–4.077	–0.000 05	+0.000 05
0.010	0.64	4.076–4.052	4.164–4.138	4.082–4.058	–0.000 12	+0.000 13
0.020	0.50	4.114–4.082	4.170–4.137	4.191–4.158	–0.000 32	+0.000 32
0.050	0.82	3.827–3.758	4.189–4.120	3.822–3.752	–0.001 75	+0.001 74
0.100	0.82	3.690–3.538	4.263–4.111	3.681–3.529	–0.007 60	+0.007 60
0.200	0.82	6.822–5.882	4.891–3.952	6.871–5.931	–0.093 99	+0.093 99
Quadratic						
0.001	2.50	4.210–4.196	4.169–4.156	4.304–4.289	–0.000 02	+0.000 01
0.002	2.50	4.137–4.115	4.175–4.151	4.110–4.089	–0.000 02	+0.000 02
0.005	2.50	4.185–4.149	4.177–4.142	4.154–4.118	–0.000 07	+0.000 08
0.010	2.50	4.144–4.108	4.177–4.140	4.128–4.091	–0.000 18	+0.000 18
0.020	2.42	4.137–4.103	4.176–4.142	4.146–4.112	–0.000 35	+0.000 34
0.050	2.50	4.137–4.097	4.168–4.128	4.148–4.108	–0.001 04	+0.001 00
0.100	2.50	4.240–4.187	4.164–4.112	4.261–4.209	–0.002 60	+0.002 62
0.200	2.50	5.459–5.118	4.294–3.952	5.424–5.083	–0.034 10	+0.034 10
Cosine						
0.001	0.75	4.413–4.368	4.167–4.146	4.307–4.270	–0.000 03	+0.000 02
0.002	0.75	4.138–4.132	4.162–4.153	4.249–4.240	–0.000 00	+0.000 01
0.005	0.82	4.206–4.180	4.171–4.146	4.129–4.103	–0.000 07	+0.000 07
0.010	0.82	4.213–4.186	4.170–4.141	4.213–4.186	–0.000 14	+0.000 14
0.020	0.82	4.128–4.093	4.173–4.138	4.104–4.070	–0.000 31	+0.000 33
0.050	0.82	4.167–4.126	4.168–4.127	4.211–4.170	–0.001 00	+0.001 00
0.100	0.82	4.269–4.212	4.159–4.102	4.283–4.226	–0.002 82	+0.002 84
0.200	0.82	6.344–5.714	4.453–3.823	6.354–5.724	–0.62 95	+0.063 00

$$\begin{aligned}
\kappa_{\text{linear}} &= [4.0 - 3.0|rt - 1.0|], \quad 0 < rt < 2 \\
\kappa_{\text{cosine}} &= [2.5 - 1.5 \cos(\pi rt)], \quad 0 < rt < 2 \\
\kappa_{\text{quad}} &= [1.5 - 0.5 \cos(\pi rt)]^2, \quad 0 < rt < 2.
\end{aligned} \tag{6.1}$$

In all three cases we characterize the time rate of change of the force constant by the rate r . Also, in every case, the switching parameter λ , which varies between 0 and 1, is equal to $(\kappa - 1)/3$.

Results for all three switching methods are given in Tables I and II. The results in Table I were generated by following a single long trajectory. At low rates, hundreds of millions of time steps, corresponding to thousands of hysteresis cycles of the force constant κ , were necessary in order to achieve three-digit accuracy. These accurate, relatively long single-trajectory simulations established that *switching times* ranging from ten to one hundred *oscillation times* are required in order for the transformation to be effectively quasistatic, with a free-energy change within $0.01NkT$ of the equilibrium value. If the increasing and decreasing portions of the coupling-parameter variations are averaged, then a time on the order of ten oscillation times suffices for a free-energy-change estimate valid within a few percent.

It was somewhat disturbing to find that the results for higher frequencies, $r = 0.2$ or 0.5 , were not only sensitive to initial conditions, but also clearly *not* ergodic. Thus, at these high rates, two simulations *differing only in the 16th digit of π* , led to quite different (30% discrepancies) predictions for the free-energy difference. Evidently, sufficiently strong deviations from equilibrium partition the phase space into disjoint parts.

In addition to the long-trajectory simulations of Table

I, we have carried out ensemble-averaged simulations, in which *many* (16 384) different initial conditions, chosen from a canonical distribution, but with the friction coefficients all 0, are first allowed to equilibrate, and are then followed in time for one or more hysteresis cycles. The ensemble data are shown in Table II. The data for the highest rate, shown there, can be roughly described by a power-law dependence on the number of cycles c :

$$\Delta A_c = \Delta A_\infty - \delta A / c^p,$$

where p is a fractional power, approximately equal to $\frac{1}{3}$.

For the lower rates, up to 0.10, the extrapolated ensemble averages agree nicely with the single-trajectory values of Table I. The good agreement between the ensemble and single-trajectory results is independent evidence that the Martyna-Klein-Tuckerman thermostats *do* sample the complete phase space.

The correct numerical value for the free-energy change using the Kirkwood-Watanabe-Reinhardt approach,

$$\Delta A / kT = N \ln 4^{1/2} = 4.159,$$

lies within about 0.01 of the numerical evaluations for the lower frequencies. The heat-based methods, using $\langle \xi_1 \Sigma(p^2/m) \rangle_\lambda$ and Σ_ξ , display noticeably larger fluctuations, suggesting that Kirkwood's approach is the best approach.

Due to the continually changing equations of motion, these systems are *not* equilibrium systems, but instead occupy nonequilibrium phase-space distributions. The Lyapunov spectra which characterize these nonequilibrium states have negative sums, reflecting the hysteresis and dissipation associated with any irreversible process

TABLE II. Ensemble-averaged free-energy changes $\Delta A_{\text{switch}}^\pm$ for cyclic six-atom Martyna-Klein-Tuckerman six-thermostat harmonic chains, with the cosine switching function $\kappa_{\text{cosine}} = [2.5 - 1.5 \cos(\pi rt)]$. The cycle time is $2/r$. Both the Kirkwood integrals and the friction-coefficient sums are displayed. The single-trajectory results from Table I are given in parentheses. The ensemble results refer to 16 384 initial conditions [with both displacements and momenta chosen from the equilibrium Maxwell-Boltzmann distribution ($kT = 1$) but with friction coefficients initially zero]. The first 40 time units were discarded. Störmer integration, with $dt = 0.005$ for rates of 0.1 and 0.2, and $dt = 0.01$ otherwise, was used. The ensemble data for the highest rate, 0.2, show that the long-time average corresponds to a power-law saturation, $\Delta A_\infty - \Delta A_c \approx c^{-p}$, where c is the number of cycles and the power p is approximately $\frac{1}{3}$.

Rate r	Cycles	$\Delta A_{\text{switch}}^\pm$	
		$\int \langle \Delta \Phi \rangle_\lambda dt$	$\int \Sigma_\xi dt$
0.020	1	4.166 - 4.128	4.127 - 4.076
0.020	(8200)	(4.173 - 4.138)	(4.104 - 4.070)
0.050	1	4.176 - 4.120	4.163 - 4.119
0.050	(20 500)	(4.168 - 4.127)	(4.211 - 4.170)
0.100	1	4.200 - 4.094	4.313 - 4.355
0.100	(41 000)	(4.159 - 4.102)	(4.283 - 4.226)
0.200	1	4.349 - 3.946	4.125 - 4.181
0.200	2	4.422 - 3.912	4.672 - 4.456
0.200	6	4.465 - 3.885	5.358 - 4.890
0.200	16	4.452 - 3.880	5.608 - 5.079
0.200	36	4.447 - 3.879	5.685 - 5.135
0.200	(82 000)	(4.453 - 3.823)	(6.354 - 5.724)

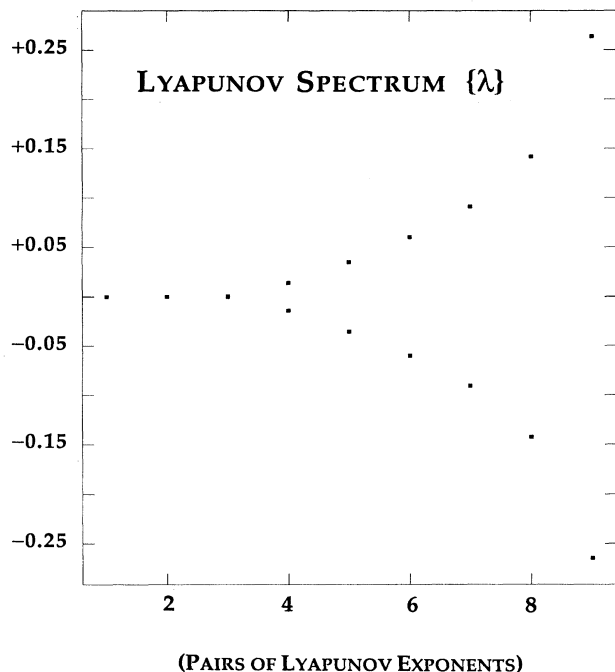


FIG. 1. Lyapunov spectrum for a thermostatted six-atom chain, with sinusoidally varying force constants, at a rate $r=0.1$. Despite the nonequilibrium nature of the system, the spectrum is nearly identical to the equilibrium one. There are 19 Lyapunov exponents in the nonequilibrium spectrum corresponding to the six coordinates, six momenta, and six friction coefficients, and the time used in our phase-space description of the motion. In the figure we show nine Smale pairs of exponents. The vanishing exponent corresponding to the time variation of the switching parameter is not included.

(and indicating the collapse of the probability density onto a multifractal strange attractor [12]), but are nevertheless very similar because the extent of the nonequilibrium behavior is so small. The loss in phase-space dimensionality, for the problems studied here, is never greater than 0.01.

As a sample we show, in Fig. 1, the Lyapunov spectrum generated using the sinusoidal switching method at a rate of $r=0.1$. All the exponents, averaged over the entire run of length 820 000, are shown in the Figure, arranged according to size. The largest and smallest ex-

ponents, the second largest and second smallest, etc., are shown as “Smale pairs” of exponents. In addition to the three vanishing exponents to be expected from fixing the center of mass, its momentum, and the lack of exponential growth in the phase-flow direction, we have found two more, so that a total of 5 of the 19 exponents vanish.

It should be noted that the apparent accuracy of the results in Ref. [3], $0.003NkT$, is literally “too good to be true.” Even in the case where those authors compared their own 108-atom results with earlier 32-atom data [4] (for which free-energy differences of order kT can confidently be expected), they reported near-perfect agreement. In fact, our own results are not at all miraculous, and appear at best only to be competitive with the (relatively many) other means for determining free energies.

VII. CONCLUSIONS

Though the present isothermal scheme loses its ergodic properties at very high driving frequencies, it behaves well at frequencies well below the particle-collision frequency. At sufficiently low frequencies all three computational routes to the free energy appear to yield equivalent results, but with a clear advantage to Kirkwood’s original work-based formulation relative to the present alternative methods. The spectacular agreement obtained previously appears to be “too good to be true.”

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