Statistical mechanical theory for non-equilibrium systems. IX. Stochastic molecular dynamics

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The general form for the probability density and for the transition probability of a nonequilibrium system is given. Maximization of the latter gives a generalized fluctuation-dissipation theorem by providing a molecular basis for Langevin’s friction force that avoids continuum hydrodynamics. The result shows that the friction coefficient must be proportional to the variance of the stochastic equations of motion. Setting the variance to zero but keeping the friction coefficient nonzero reduces the theory to a Hoover thermostat without explicit constraint, although such a limit violates the physical requirement of proportionality between the dissipation and the fluctuation. A stochastic molecular dynamics algorithm is developed for both equilibrium and nonequilibrium systems, which is tested for steady heat flow and for a time-varying, driven Brownian particle. © 2009 American Institute of Physics. [DOI: 10.1063/1.3138762]

I. INTRODUCTION

Computer simulations are in principle exact and they provide reliable, quantitative data for realistic models, as well as benchmark results to test approximate theories. The two main equilibrium simulation techniques are Monte Carlo and molecular dynamics.¹ Monte Carlo for an equilibrium canonical system samples the Boltzmann distribution and yields averages appropriate for an equilibrium subsystem in thermal contact with a constant temperature reservoir. Other Gibbsian reservoirs (e.g., constant pressure and constant chemical potential) can also be simulated.¹ The simplest equilibrium molecular dynamics algorithm uses Hamilton’s equations of motion alone, which would be appropriate for a microcanonical or adiabatic system, but numerical errors lead to a slow increase in system temperature as the system evolves to higher entropy states.² For this reason a thermostat is generally employed, with one of the earliest and still relatively common being the Hoover isokinetic thermostat, which adds a deterministic friction term to Hamilton’s equations.³ The kinetic energy is generally used for the thermostat, although the configurational temperature has also been used.⁴ The problem with this is that it does not generate averages that correspond to the Boltzmann distribution.

The so-called Nosé-Hoover thermostat⁴ and Nosé-Hoover chain thermostat⁷ augment the subsystem phase space with an extra variable or variables in such a way that ensures the equilibrium Boltzmann distribution on the subsystem phase space alone. A modified form of the Nosé thermostat has also been used in nonequilibrium simulations.⁸ The equations of motion on the extended phase space are deterministic, but obviously they are stochastic when considered on the subsystem phase space alone (i.e., the coordinates of the lower space alone do not uniquely determine its evolution). The distinction between deterministic and stochastic equations of motion is rather important in this paper.

Andersen⁹ gave a stochastic thermostat for equilibrium molecular dynamics, which has been variously modified and tested.¹⁰–¹² Attard² and Boinepalli and Attard¹³ combined molecular dynamics with a stochastic transition probability. These stochastic thermostats are designed to sample the equilibrium Boltzmann distribution (or its equilibrium Gibbsian generalizations).

For nonequilibrium systems, the subject of the present series of papers, (reviewed in Ref. ¹⁴), reliable simulation algorithms are virtually nonexistent. Obviously any algorithm that is designed to sample the equilibrium Boltzmann distribution cannot be relied on for a nonequilibrium system; the demands of nonequilibrium simulations require purpose built methods that satisfy additional criteria, including the requirement that they must not yield the equilibrium Boltzmann distribution. (Applying the thermostat only to atoms in a boundary reservoir may possibly alleviate the problem.)¹⁵ The recent discovery of the nonequilibrium probability distribution led to the development of a nonequilibrium Monte Carlo (NEMC) algorithm, which has been successfully tested by application to steady heat flow.¹⁶

The so-called nonequilibrium molecular dynamics algorithm (NEMD) has also been applied to the problem of steady heat flow and to other nonequilibrium systems.¹,¹⁷ However this method uses the deterministic Hoover isokinetic thermostat (and other artificial non-Hamiltonian terms) and it therefore samples neither the equilibrium Boltzmann distribution nor the correct nonequilibrium distribution. While the NEMD method may not be a bad approximation in the linear response regime, it cannot be relied upon in regimes where it has not been tested by exact methods. Of course the main argument in favor of computer simulations is that they produce exact results in any regime and, unfortunately, this cannot be said of the NEMD method.

This paper derives the transition probability for general
nonequilibrium systems and uses it to develop a stochastic molecular dynamics (SMD) algorithm, improving an earlier nonequilibrium SMD algorithm. One notable result is a variational principle that provides a generalized fluctuation-dissipation theorem. The result takes the form of a molecular version of Stokes’ law and provides a fundamental justification for the functional form of the Hoover thermostat. The theorem shows that the friction coefficient must be proportional to the strength of the stochastic part of the equations of motion induced by the reservoir. The corollary is that deterministic, thermostatted equations of motion are unphysical. The SMD algorithm is tested for steady heat flow and for a solute in a moving potential trap.

II. ANALYSIS

A. Probability density

The nonequilibrium probability density in the subsystem phase space is formally

$$\varphi(\Gamma, t) = e^{\beta S_{\text{eq}}(\Gamma, t)/k_B} Z(t).$$

(2.1)

Here $\Gamma = \{q^N, p^0\}$ is a point in the subsystem phase space, $t$ is time, $Z(t)$ is the partition function, which normalizes the probability density to unity, and $k_B$ is Boltzmann’s constant. The reservoir entropy, which appears in the exponent because phase space has no internal entropy, formally comprises an equilibrium and a nonequilibrium part,

$$S(t) = S_{\text{eq}}(\Gamma, t) + S_{\text{ne}}(\Gamma, t).$$

(2.2)

The equilibrium part is that part of the reservoir entropy that would exist if the system had no memory. For example, for a mechanical nonequilibrium system in contact with a thermal reservoir of temperature $T$, in which the subsystem Hamiltonian has an explicit time dependence, $H(\Gamma, t)$, the equilibrium part of the reservoir entropy is

$$S_{\text{eq}}(\Gamma, t) = - k_B T \left( \frac{n(\Gamma, t)}{N} \right)^T,$$

(2.3)

where $\beta = 1/k_B T$. For a thermodynamic nonequilibrium system, such as steady heat flow, one has

$$S_{\text{eq}}(\Gamma, t) = - k_B T \left( \frac{n(\Gamma, t)}{N} \right)^T - \beta_0 E_0(\Gamma) - \beta_1 E_1(\Gamma).$$

(2.4)

This is the structural part of the reservoir entropy discussed in Paper I, in which the $\beta_i$ are the zeroth and first inverse temperatures, which in essence respectively correspond to the average and to the gradient of the reservoir temperature, and the $E_i$ are the conjugate zeroth and first energy moments of the subsystem. In the general case, the equilibrium part of the reservoir entropy is insensitive to the direction of time,

$$S_{\text{eq}}(\Gamma, t) = S_{\text{eq}}(\Gamma^T, t),$$

(2.5)

where the conjugate phase space point has the momenta reversed, $\Gamma^T = (q^N, (-p)^0)$.

The non-equilibrium part of the reservoir entropy removes the adiabatic contribution to the change in the equilibrium part of the reservoir entropy.

$$S_{\text{ne}}(\Gamma, t) = - \int_{t_0}^t dt \frac{\delta^{\text{eq}}}{\delta t} \left( \bar{F}(\Gamma|t), t' \right).$$

(2.6)

Here $\bar{F}(\Gamma|t)$ is the most likely trajectory proceeding backward in time from the current point in phase space (see Sec. III). For a long enough trajectory the two termini are uncorrelated and the nonequilibrium part of the reservoir entropy has at most a trivial dependence on $t_0$.

By design, the most likely rate of change is

$$\dot{S}_{\text{ne}}(\Gamma, t) = - S_{\text{eq}}(\Gamma, t).$$

(2.7)

Hence $\dot{S}_{\text{ne}}(\Gamma, t) = - \dot{S}_{\text{eq}}(\Gamma, t)$, which defines the equilibrium part of the reservoir entropy. This of course is how the expression for the reservoir entropy was arrived at. It is just Newton’s third law: the reservoir entropy can only change via the force that it exerts on the subsystem.

The adiabatic derivative here and throughout is that of an isolated subsystem, and is denoted by a superscript 0,

$$\dot{S}_{\text{eq}}(\Gamma, t) = \frac{\partial S_{\text{eq}}(\Gamma, t)}{\partial t} + \dot{H}(\Gamma, t) \cdot \nabla S_{\text{eq}}(\Gamma, t),$$

(2.8)

with the adiabatic equations of motion being Hamilton’s,

$$\dot{q}^0 = \frac{\partial H(\Gamma, t)}{\partial p}, \quad \dot{p}^0 = - \frac{\partial H(\Gamma, t)}{\partial q}. $$

(2.9)

Since adiabatic means isolated from a reservoir, then an adiabatic subsystem must necessarily evolve according to the subsystem Hamiltonian.

The nonequilibrium part of the reservoir entropy is sensitive to the direction of time,

$$S_{\text{ne}}(\Gamma, t) \neq S_{\text{ne}}(\Gamma^T, t).$$

(2.10)

To a good approximation, it may be replaced by its odd, adiabatic projection,

$$S_{\text{ne}}(\Gamma, t) \approx S_{\text{ne}}(\Gamma^T, t) \approx S_{\text{ne}}^{\text{odd}}(\Gamma, t),$$

(2.11)

where the superscript 0 signifies that the most likely trajectory in the integrand has been replaced by the adiabatic trajectory. Differentiating the probability density normalization, $\int d\Gamma \varphi(\Gamma, t) = 1$, shows that

$$\frac{\dot{Z}(t)}{Z(t)} = \left( \frac{\delta S_{\text{ne}}(\Gamma, t)}{k_B} \right)_t = \left( \frac{\dot{S}_{\text{ne}}(\Gamma, t)}{k_B} \right)_t. $$

(2.12)

The second equality follows by writing the integrand in terms of the adiabatic development. These two results imply that

$$\langle \nabla S_{\text{ne}}(\Gamma, t) \rangle_t = 0.$$ (2.13)

Equations (2.2) and (2.7) can be rearranged as

$$\dot{S}_{\text{ne}}(\Gamma, t) = - \frac{\delta S_{\text{ne}}(\Gamma, t)}{\partial t} - \Delta^{-1} \nabla \cdot p S_{\text{ne}}(\Gamma, t).$$

(2.14)

Since on the average the left hand side vanishes, this yields
This will be used as a constraint on the most likely reservoir perturbation.

The expression for the rate of entropy production is not simply related to the compressibility of phase space that arises from the deterministic, non-Hamiltonian part of the equations of motion. Such a nonzero compressibility has been interpreted by some to correspond to the rate of entropy production, which interpretation has been criticized in detail.

**B. Transition probability**

Now the probability of the transition $\Gamma_1 \rightarrow \Gamma_4$ in time $t \rightarrow t'=t+\Delta t$ is given. This is composed of the adiabatic transition to $\Gamma_2 = \Gamma_1 + \Delta \Gamma^0$, and the reservoir perturbation, $\Gamma_4 = \Gamma_2 + \mathbf{R}$. One can write $\mathbf{R} = \mathbf{\tilde{R}} + \mathbf{\tilde{R}}$, where $\mathbf{R}$ is the most likely perturbation and $\mathbf{\tilde{R}}$ has mean zero and variance $\sigma^2 \tilde{\Delta}_i^2 \tilde{\gamma}_i$. The reservoir perturbation is a stochastic force (i.e., it has only momentum components) and so the equations of motion to linear order in the time step are

$$p_{i\alpha}(t+\Delta t) = p_{i\alpha}(t) + \Delta \tilde{p}_{i\alpha}(t) + \mathbf{\tilde{R}}_{\alpha}(t),$$

$$q_{i\alpha}(t+\Delta t) = q_{i\alpha}(t) + \Delta \tilde{q}_{i\alpha}(t).$$

The most likely reservoir perturbation remains to be determined.

The general nonequilibrium theory, presented by the author in the present series of papers and reviews, is based on the concept of second entropy, which is the entropy of a transition and whose exponential gives the probability of a transition. In the second entropy one can identify two terms: the first corresponds to the change in the subsystem macrostate and the second corresponds to half the change in the first entropy of the macrostate of the total system (subsystem plus reservoir). This second term, including the factor of one half, is fixed by the formally exact reduction condition.

The present problem is of a transition in the subsystem phase space, which as a phase space has no subsystem entropy associated with it. Hence the only term that contributes to the second entropy of a phase space transition is half the change in the reservoir entropy. The change in the most likely reservoir entropy due to the transition is

$$S_r(\Gamma_4,t') = S_r(\Gamma_1,t) = \Delta S^0_r(\Gamma_1,t) + \mathbf{R} \cdot \nabla p S_r(\Gamma_1,t),$$

with $S_r$ as the estimate based upon the most likely trajectory, Eqs. (2.2) and (2.6). In fact, the formally exact change in the actual reservoir entropy is

$$\Delta S_r = \mathbf{R} \cdot \nabla p S_{eq}(\Gamma_1,t).$$

The second entropy for the transition consists of half this change in the most likely reservoir entropy, plus a stochastic term of variance $\sigma$, 

$$S^{(2)}(\Gamma_4,t';\Gamma_1,t) = -\frac{k_B}{2\sigma} \mathbf{R} \cdot \mathbf{R} + \frac{1}{2} \mathbf{R} \cdot \nabla p S_r(\Gamma_1,t)$$

$$+ \frac{\Delta t}{2} S^0_r(\Gamma_1,t).$$

One expects that all stochastic perturbations are encompassed by such a quadratic form (cf., the central limit theorem). The variance represents the strength of the coupling between the subsystem and the reservoir. This form of the second entropy for the phase space transition is in essence the same as that given in Ref. 18, except that there the change in the actual reservoir entropy was used. This second entropy can be generalized to the path entropy and used to derive the fluctuation and work theorems.

Exponentiating the second entropy gives the conditional transition probability,

$$\rho(\Gamma_4,t'|\Gamma_1,t) = e^{-\mathbf{R} \cdot \mathbf{R}/2\sigma} \frac{S_r(\Gamma_4,t') - S_r(\Gamma_1,t)}{2k_B}$$

$$= e^{-\mathbf{R} \cdot \mathbf{R}/2\sigma} \frac{\mathbf{R} \cdot \nabla p S_r(\Gamma_1,t)}{2k_B} \Delta S^0_r(\Gamma_1,t)/2k_B.$$

The adiabatic change in the reservoir entropy, the final exponent, does not depend on $\mathbf{R}$ and can be incorporated into the normalization factor.

The normalizing factor is

$$\xi(\Gamma_1,t) = \frac{\mathbf{R} - \mathbf{\tilde{R}}}{2k_B} e^{-\mathbf{R} \cdot \mathbf{R}/2\sigma} \left[ 1 + \frac{\mathbf{R} \cdot \nabla S_{r,1}}{2k_B} + \frac{\mathbf{R} \cdot \nabla S_{r,1}^2}{8k_B} \right] + \delta \Delta S^0_r(\Gamma_1,t)/2k_B$$

$$+ (2\pi\alpha)^{3/2} \frac{\sigma}{8k_B} \frac{\nabla p S_{r,1}}{4k_B} \frac{\nabla p S_{r,1}}{4k_B}$$

$$+ \Delta t \Delta S^0_r(\Gamma_1,t)/2k_B + O(\Delta t^2),$$

where $S_{r,1} = S_r(\Gamma_1,t)$. Retaining the quadratic terms prior to integration gives the final result to $O(\sigma)$ and to $O(\Delta \gamma)$. Note that this and all of the following results are valid to linear order in the time step. The space- and time-dependent parts of $\xi(\Gamma,t)$ are linearly proportional to $\alpha \gamma \Delta \gamma$ and so

$$\xi(\Gamma_4,t') = \xi(\Gamma_1,t) + \mathbf{R} \cdot \nabla \xi(\Gamma_1,t)$$

$$+ \Delta t \partial_t \xi(\Gamma_1,t)/\partial t_1 = \xi(\Gamma_1,t) + O(\Delta t^2).$$

The consistency between this transition probability and the nonequilibrium probability density is assured, since
\[ \int d\Gamma_1 \rho(\Gamma_4, t') \rho(\Gamma_1, t) = \frac{e^{S^{(2)}_{\rho} + \hat{H}_B}}{Z(t)} \int d\Gamma_1 e^{-R e^{2\sigma} R e^{2\sigma}} e^{\hat{H}_B} e^{S_{\rho}^{(2)}} = \rho(\Gamma_4, t') \frac{Z(t)}{Z(t')} \int d\Gamma_2 e^{-R e^{2\sigma} R e^{2\sigma}} e^{\hat{H}_B} e^{S_{\rho}^{(2)}} = \rho(\Gamma_4, t') \frac{Z(t)}{Z(t')} \xi_4^2(\Delta_t) = \rho(\Gamma_4, t'). \tag{2.23} \]

The second equality exploits the unity of the Jacobian of the adiabatic transformation. The final equality holds on average since it uses Eq. (2.12). It also uses the fact that \( \xi(\Gamma_1, t, -\Delta_t) = \xi(\Gamma_1, t, \Delta_t) e^{-\Delta_t \Delta_t(\Gamma_1, t) + O(\Delta_t^2)}. \) One concludes from this that the transition probability, Eq. (2.20), preserves the nonequilibrium probability.

### C. Most likely trajectory

#### 1. General nonequilibrium case

A formal expression for the most likely reservoir perturbation follows by maximizing the second entropy, Eq. (2.19), \( \partial S^{(2)} / \partial R = 0, \) with solution

\[ \bar{R} = \frac{\sigma}{2k_B} \nabla_{\rho} S_{\rho}^{(2)}(\Gamma, t) + \frac{\mu}{2k_B} \nabla_{\rho} S_{\rho}(\Gamma, t). \tag{2.24} \]

The nonequilibrium part of the reservoir entropy makes this nontrivial to evaluate.

Now write \( \nabla_{\rho} S_{\rho} \) as a linear combination of an even and an odd parity term,

\[ \nabla_{\rho} S_{\rho}(\Gamma, t) = \eta \nabla_{\rho} S_{\rho}^{(2)}(\Gamma, t) + \mu \nabla_{\rho} S_{\rho}^{(0)}(\Gamma, t). \tag{2.25} \]

The two constraints that will be enforced below are a linear combination of these two gradients. Hence this ansatz may be interpreted as maximizing the formally exact form of the second entropy, \( S^{(2)} = -k_B R / 2 \sigma + R \cdot \nabla_{\rho} S_{\rho} / 2, \) subject to the two constraints given below, with \( \eta \) and \( \mu \) representing Lagrange multipliers.

With this approximation to \( \nabla_{\rho} S_{\rho}^{(2)} \), the nontrivial part of the second entropy, Eq. (2.19), becomes

\[ S^{(2)}(\Gamma, \Delta_t) = -\frac{k_B}{2} R \cdot R + \frac{1 + \eta}{2} R \cdot \nabla_{\rho} S_{\rho}^{(2)}(\Gamma) + \frac{\mu}{2} R \cdot \nabla_{\rho} S_{\rho}^{(0)}(\Gamma). \tag{2.26} \]

Maximizing this gives the most likely reservoir perturbation,

\[ \bar{R}(\Gamma, t) = \frac{\sigma}{2k_B} [1 + \eta] \nabla_{\rho} S_{\rho}^{(2)}(\Gamma, t) + \frac{\sigma \mu}{2k_B} \nabla_{\rho} S_{\rho}^{(0)}(\Gamma, t). \tag{2.27} \]

The first constraint to be satisfied is Eq. (2.15),

\[ \bar{R}(\Gamma, t) \cdot \nabla_{\rho} S_{\rho}(\Gamma, t) = -\Delta_t k_B Z(t)/Z(t). \tag{2.28} \]

This is stronger than is actually required as it only has to hold on average.

The second constraint is to keep the reservoir perturbation orthogonal to the adiabatic flux,

\[ \bar{R}(\Gamma, t) \cdot \nabla_{\rho} S_{\rho}^{(0)}(\Gamma, t) = 0. \tag{2.29} \]

It will be shown in the simulation results reported below that if this constraint is not imposed then the resultant flux is lower than it ought to be due to the stochastic perturbation diminishing the adiabatic order that naturally develops. In a sense this constraint reflects Onsager’s regression hypothesis, namely, that the adiabatic flux that develops following a fluctuation in the static structure of an isolated system is the same as the flux that is present when that static structure is imposed by a reservoir. One should therefore minimize the disturbance of the internal adiabatic flux by the reservoir perturbation. In a real physical system this is accomplished by the reservoirs being located at the boundaries and therefore they cannot perturb the bulk of the subsystem. In the present formulation of the problem in which the reservoirs are idealized, the whole subsystem feels the influence of the reservoirs, and so this constraint enforces the physical condition that the adiabatic flux must be negligibly perturbed by the reservoirs.

In order to determine the Lagrange multipliers from the two constraints, it is convenient to define

\[ c_1 = \eta \nabla_{\rho} S_{\rho}^{(2)}(\Gamma, t) / k_B, \]

\[ c_2 = \frac{\sigma \mu}{2} \nabla_{\rho} S_{\rho}^{(0)}(\Gamma, t) / k_B, \tag{2.30} \]

and \( D = c_1 c_3 - c_2^2. \) With these the first constraint becomes

\[ \frac{\sigma}{2} [1 + \eta] c_1 + \frac{\sigma \mu}{2} c_2 = -\Delta_t \hat{Z}(t)/Z(t), \tag{2.31} \]

and the second is

\[ \frac{\sigma}{2} [1 + \eta] c_2 + \frac{\sigma \mu}{2} c_3 = 0. \tag{2.32} \]

These have solution

\[ \eta = -2 c_1 c_3 \hat{Z}(t)/\sigma D Z(t), \tag{2.33} \]

assuming \( \eta \approx 1, \) and

\[ \mu = -[1 + \eta] c_2 / c_3. \tag{2.34} \]

Experience shows that in practice \( \eta \) is negligible and that it affects significantly neither the flux nor the structure.

It may be mentioned that these equations of motion are
not reversible in the sense that if $\Gamma_2 = \overline{\Gamma}(t+\Delta_1|\Gamma_1, t)$, then $\Gamma_1 \neq \overline{\Gamma}(t-\Delta_1|\Gamma_2, t)$. This is due to the fact that the most likely perturbation contains a term proportional to $|\Delta_1|$, which does not reverse sign when $\Delta_1$ is reversed. Neither do the equations obey Hamiltonian conjugacy, since $\overline{\Gamma}(\Gamma^*) \neq -[\overline{\Gamma}(\Gamma)]^*$, which means that $\Gamma_1^* \neq \overline{\Gamma}(t+\Delta_1|\Gamma_2, t)$. Irreversibility is of course mandatory in nonequilibrium thermodynamics.

2. Most likely trajectory for an equilibrium system

For the canonical equilibrium system, $S_{eq}(\Gamma, t) = -\mathcal{H}(\Gamma)/T$. The adiabatic derivative vanishes due to the constancy of the energy, $S^0_{eq}(\Gamma, t) = 0$, and hence the nonequilibrium part of the reservoir entropy is zero. The second entropy in this case is therefore

$$S^{(2)}(R|\Gamma) = \frac{-k_B}{2\sigma} \mathbf{R} \cdot \mathbf{R} - \frac{1}{2T} \mathbf{R} \cdot \nabla_p \mathcal{H}(\Gamma)$$

$$= \frac{-k_B}{2\sigma} \sum_i R^2_{ia} - \frac{1}{2T} \sum_i \frac{\dot{R}_{ia} \dot{p}_{ia}}{m_i},$$

(2.35)

where $m_i$ is the mass of atom $i$. Since the constraint $\mathbf{R} \cdot \nabla_p S^0_{eq} = 0$ is automatically satisfied, one can maximize this unconstrainedly to obtain the most likely reservoir perturbation,

$$\dot{R}_{ia} = -\frac{\beta \sigma}{2m_i} p_{ia}.$$  \hspace{1cm} (2.36)

The corresponding equilibrium equations of motion are

$$p_{ia}(t+\Delta_1) = p_{ia}(t) + \Delta \dot{p}_{ia}(t) - \frac{\beta \sigma}{2m_i} p_{ia} + \dot{R}_{ia}(t),$$

$$q_{ia}(t+\Delta_1) = q_{ia}(t) + \Delta \dot{q}_{ia}(t),$$

(2.37)

where $\dot{R}_{ia}(t)$ is a random variable of mean zero and variance $\sigma$. It can be shown explicitly that the Boltzmann distribution is stationary under these stochastic equations of motion to linear order in the time step.\(^\dagger\)

The most likely reservoir perturbation appears as a drag or friction force, with friction coefficient $\beta \sigma / 2$. Interestingly enough this is the same functional form as a Hoover thermostat, but with several crucial differences.

First, the friction coefficient is not arbitrary. It cannot be determined, for example, by enforcing an isokinetic constraint.

Second, one cannot have deterministic, non-Hamiltonian equations of motion, at least not with a thermostat with this functional form. If the variance is set to zero, then necessarily the friction coefficient must also be zero. Conversely, a nonzero Hoover-like thermostat necessitates stochastic equations of motion with variance related to the friction coefficient in the above fashion. (The Hoover friction coefficient arising from an isokinetic or similar constraint varies slowly in phase space. Because this variation can be neglected in the thermodynamic limit, it is legitimate to make the comparison with the deterministic limit of the present theory in which the friction coefficient is a constant.) In other words, deterministic, non-Hamiltonian equations of motion violate the fluctuation-dissipation theorem.

Third, and perhaps of most long term significance, this result represents a generalization of the fluctuation-dissipation theorem, in the sense that it derives the friction force law as the functional form for the dissipation. As in the original version of the fluctuation-dissipation theorem derived by Langevin, the friction coefficient has to be proportional to the variance, which controls the fluctuations. The present result is a generalization because this rule applies at the molecular level, whereas Langevin’s original justification was purely macroscopic: the functional form chosen as the friction or drag force was justified by appealing to Stokes’ law of linear hydrodynamics. The present derivation shows that the fluctuation-dissipation theorem is purely a molecular law that has its basis in statistical mechanics and it is not restricted to linear hydrodynamics or to macroscopic particles.

3. Most likely trajectory for mechanical work

In the case of mechanical work, the equilibrium part of the reservoir entropy is proportional to the Hamiltonian, $S_{eq}(\Gamma, t) = -\mathcal{H}(\Gamma, t)/T$, and so the adiabatic derivative of the Hamiltonian is independent of the momenta, $\dot{\mathcal{H}}(\Gamma, t) = \partial U_{eq}(q^N, t)/\partial t$. From these results it follows that the momentum gradient of the adiabatic flux vanishes,

$$\nabla_p S_{eq}(\Gamma, t) = 0.$$  \hspace{1cm} (2.38)

Hence one can take the momentum derivative of the dynamic part of the reservoir entropy to be proportional to the momentum derivative of the static part of the reservoir entropy alone,

$$\nabla_p S_{eq}(\Gamma, t) = \eta \nabla_p S_{eq}(\Gamma, t).$$

(2.39)

The constraint yields

$$\eta = \frac{-2\Delta Z(t)}{\sigma \Gamma_1 Z(t)} \to 0.$$  \hspace{1cm} (2.40)

In the case that the mechanical work is done on a solute at vanishing concentration, this vanishes in the thermodynamic limit since $\Gamma_1$ is an extensive variable that scales with the system size [whereas $Z(t)/Z(t)$ is intensive as it scales with the solute].

Now the momentum derivative in the case of mechanical work is explicitly

$$\frac{\partial S_{eq}(\Gamma, t)}{k_B \partial p_{ia}} = -\frac{\beta p_{ia}}{m_i},$$

(2.41)

from which the most likely reservoir perturbation follows,

$$\dot{R}_{ia} = -\frac{\beta \sigma}{2m_i} [1 + \eta] p_{ia} \to -\frac{\beta \sigma}{2m_i} p_{ia}.$$  \hspace{1cm} (2.42)

This has the same functional form as in the equilibrium case. Again the friction coefficient is related to the strength of the stochastic perturbations by the generalized fluctuation-dissipation theorem. That the reservoir perturbations in this
nonequilibrium case are the same as in the equilibrium case appears to be a consequence of the intensive nature of the mechanical work in this particular model. The result suggests that any thermostat that corresponds to the canonical Boltzmann distribution will yield correct results for a nonequilibrium system with intensive time-dependent work.

4. Most likely trajectory for steady heat flow

Consider two thermal reservoirs of temperatures $T_\pm$ sandwiching a subsystem with which they can exchange energy across boundaries located at $z=\pm L/2$. The zeroth and first inverse temperatures are

$$
\beta_0 = \frac{1}{k_B} \left[ \frac{1}{T_+} + \frac{1}{T_-} \right], \quad \beta_1 = \frac{1}{k_B L} \left[ \frac{1}{T_+} - \frac{1}{T_-} \right].
$$

(2.43)

The conjugate thermodynamic variables are the energy moments, those of the subsystem are denoted as $E_0(\Gamma)$ and $E_1(\Gamma)$. The zeroth moment is of course just the total energy of the subsystem and its adiabatic derivative vanishes. The adiabatic derivative of the first energy moment is nonzero, $\dot{E}_1(\Gamma) \neq 0$, and its average value gives the heat flux through the subsystem.

The equilibrium part of the reservoir entropy is

$$
S_{eq}(\Gamma,t) = -\beta_0 E_0(\Gamma) - \beta_1 E_1(\Gamma).
$$

(2.44)

Hence

$$
\frac{\delta S_{eq}(\Gamma)}{k_B \partial p_{ia}} = -\frac{\beta_0}{m_i} p_{ia} + \frac{\beta_1}{m_i} \dot{z}_i = -\frac{\beta_0}{m_i} p_{ia} + \frac{\beta_1 (z) p_{ia}}{m_i},
$$

(2.45)

with $\beta(z) = \beta_0 + \beta_1 z$. The adiabatic flux may be written as

$$
\dot{S}_{eq}(\Gamma)/k_B = -\beta_1 \dot{E}_1(\Gamma) = -\beta_1 \sum_{ia} \kappa_{ia} p_{ia},
$$

(2.46)

with

$$
\kappa_{ia} = \frac{\epsilon_i}{m_i} \delta_{a,z} - \sum_j j^x u'(q_{ij}) q_{ia} - q_{ja} \frac{1}{2m_i q_{ij}},
$$

(2.47)

which invokes the energy of atom $i$,

$$
\epsilon_i = \frac{p_i^2}{2m_i} + w(q_{iz}) + \sum_{j=1}^N j^y u(q_{ij}),
$$

(2.48)

where $w$ is the wall potential, if present, and $u$ is the pair potential. Hence the momentum derivative of the flux is

$$
\frac{\delta \dot{S}_{eq}(\Gamma)}{k_B \partial p_{ia}} = -\beta_1 \left[ \kappa_{ia} + p_{ic} p_{ia}/m_i^2 \right].
$$

(2.49)

With these the most likely reservoir perturbation is explicitly

$$
\dot{R}_{ia} = \frac{\beta(z) \sigma [1 + \eta]}{2m_i} p_{ia} - \beta_1 \sigma \mu \frac{\kappa_{ia} + p_{ic} p_{ia}/m_i^2}{2}.
$$

(2.50)

The first term could be interpreted as a generalized friction force.

The coefficients $\eta$ and $\mu$ were given above: $\mu = [1 + \eta](c_2/c_3$ and $\eta = -2\Delta c_2 Z(t)/\sigma D Z(t)$. In the present case,

$$
c_1 = \sum_{ia} \frac{\beta(z)_{ia}^2}{m_i^2} p_{ia}^2,
$$

$$
c_2 = \beta_1 \sum_{ia} \frac{\beta(z) p_{ia}}{m_i} \left[ \kappa_{ia} + p_{ic} p_{ia}/m_i^2 \right],
$$

(2.51)

$$
c_3 = \beta_1^2 \sum_{ia} \left[ \kappa_{ia} + p_{ic} p_{ia}/m_i^2 \right]^2,
$$

and $D = c_1 c_3 - c_2^2$. The logarithmic derivative of the partition function is

$$
\frac{\dot{Z}(t)}{Z(t)} = -k_B \tilde{S}_0/e = \beta_1 \tilde{E}_1.
$$

(2.52)

In a practical simulation, the instantaneous value of $\beta_1 \tilde{E}_1(\Gamma)$ is used to evaluate this. Fourier’s law gives the thermal conductivity as $\lambda = \beta_1 \tilde{E}_1$, where $V$, the volume of the subsystem, and the average adiabatic flux is used to evaluate the right hand side.

III. COMPUTER SIMULATION RESULTS

A. Steady heat flow

1. System details

Nonequilibrium SMD simulations have been performed for a Lennard-Jones fluid. Results are reported in dimensionless form by invoking the well-depth $\epsilon_{LJ}$, the diameter $\sigma_{LJ}$, and the time constant $\tau_{LJ} = \sqrt{\mu_{LJ} \sigma_{LJ}^2 / \epsilon_{LJ}}$, where $\mu_{LJ}$ is the mass, and by setting Boltzmann’s constant to unity. The pair potential was cut off at $R_{cut}=2.5$, $u_{cut}(r)=0$, $r \geq R_{cut}$, and shifted within the cutoff, $u_{cut}(r)=u(r)-u(R_{cut})$, $r \leq R_{cut}$. No tail correction was invoked. As detailed in Ref. 20, a spatial neighbor table with cubic cells of side length $\approx 0.6$ was used, which is about three times more efficient than the conventional method that uses $R_{cut}$.

A slit pore was simulated, which had uniform Lennard-Jones walls normal to the $z$-axis, with uniform bulk density in the center of the cell. Periodic boundary conditions and the minimum image convention were used in the lateral directions.

Fourier’s law shows that the adiabatic relaxation of the first energy moment leads to a temperature profile with zero gradient at the walls, because there is no heat flux across the boundaries. Hence in the present slit pore, the adiabatic part of the motion counteracts at the boundaries the linear temperature profile that the reservoir perturbation seeks to impose (see results). This also affects the dynamics in the vicinity of the walls. For this reason, when calculating the rate of change of energy moment and also when calculating the $\eta$ and the $\mu$, only the contribution from atoms in the central half of the slit pore was used.

Generally 800 atoms were used, with the lateral width being $L_x=5.87$, and, in the case of $\rho=0.8$, the nominal distance between the walls being $L_z=29.87$, which gave a fluid phase width of $L_z=28.55$. For this case, the temperature of the reservoirs were $T_+ = 2.25$ and $T_+ = 1.80$, which correspond to $T_0 = 2$ and $\beta_1 = 3.7 \times 10^{-3}$.
Most of the results presented below were obtained with a time step of $\Delta t = 5 \times 10^{-3}$. No change was observed upon reducing this to $2 \times 10^{-3}$. Past experience has shown that a time step larger than $7.5 \times 10^{-3}$ for these systems with these equations of motion causes the kinetic energy to increase significantly on an adiabatic trajectory.

A dimensionless variance was defined, $\sigma^2 = 2\sigma m_k k_B T_0$, where the denominator is the average of the square of a component of the momentum. Values of $\sigma^2 \sim 1$ mean that the stochastic change in a momentum component is of the same order as the momentum component itself.

A time step consists of an adiabatic part and a reservoir perturbation, as described below. In most of the results reported here averages were collected every 100 time steps. In some cases this was reduced to every 10 time steps, which appeared statistically more efficient.

### 2. Algorithm

The adiabatic and stochastic steps were alternated. In the adiabatic step all the atoms were moved according to second order equations of motion

$$ q_{iad}(t + \Delta t) = q_{iad}(t) + \Delta q_{iad}(t) + \frac{\Delta^2}{2m} F_{iad}(t), $$

$$ p_{iad}(t + \Delta t) = p_{iad}(t) + \frac{\Delta}{2} [F_{iad}(t) + F_{iad}(t + \Delta t)], $$

where $F_{iad}(t) = F_{iad}(q^N(t))$ and $F_{iad}(t+\Delta t) = F_{iad}(q^{0,N}(t+\Delta t))$ are the force.

In the stochastic step, the positions were kept fixed at their values following the adiabatic transition, and all the momenta were changed according to

$$ p_{iad}(t + \Delta t) = p_{iad}(t + \Delta t) + \vec{R}_{iad}(t) + \vec{R}_{iad}(t). $$

The expression for the most likely reservoir perturbation, $\vec{R}_{iad}(t)$, was given in Sec. II C 4.

### 3. Results

The local temperature $T(z)$ is shown in Fig. 1 for two values of the variance. The local kinetic energy was used as the equipartition theorem can be shown to hold for steady heat flow.\(^{14}\) The profiles have approximately zero gradient at the boundaries, as is most evident in the system with the lower variance. Small values of the variance mean that the adiabatic evolution dominates and the zero heat flux across the walls lead to the zero gradient. Conversely, a large variance means that sufficient heat can be supplied by the reservoirs to overcome this effect.

The data in Fig. 1 also show that the induced temperature gradient is less than the applied temperature gradient at low values of the variance. Again this is because the adiabatic relaxation of the first energy moment corresponds to heat flow from the high energy region of the subsystem to the low energy region, and this internal heat flow is proportional to the induced temperature gradient. In the steady state this internal heat flow must be canceled by the heat flow from the reservoirs, the rate of which is controlled by the variance. Hence a low variance implies a small heat flow, which implies a reduced induced temperature gradient, as Fig. 1 confirms.

Figure 2 shows the dependence of the kinetic temperature, averaged over the whole system and normalized to the zeroth temperature, on the variance. The derivation of the transition probability relied upon an expansion to linear order in $\sigma$. Neglecting the quadratic terms is obviously not valid for larger values of $\sigma$, which is the likely cause of the increase in temperature with increasing variance revealed in the figure.

That the normalized temperature is slightly greater than unity for small variance appears to be a second order effect that arises in averaging the temperature over the whole system. The applied temperature profile for small gradients may be expanded as

$$ k_B T(z) = \frac{1}{\beta_0 + z\beta_1} = \beta_0 \left[ 1 - \frac{\beta_1}{\beta_0} z + \frac{\beta_2}{\beta_0^2} z^2 + \cdots \right]. $$

Integrating this over the slit pore gives $T_0 = T_0 [1 + (\beta_1/\beta_0^2) L_z^2/12]$. This equals 1.004$T_0$ for the parameters of Fig. 2, which is in reasonable agreement with the low variance data.

As was discussed in connection with Fig. 1, the induced temperature gradient is less than it should be when the cou-
pling between the subsystem and the reservoir is too weak to supply heat fast enough to compensate for the adiabatic relaxation of the energy moment. This effect is shown quantitatively in Fig. 3. The temperature gradient here and below is measured in the central half of the slit pore. For \( \sigma^2 \approx 0.002 \), it can be seen that the induced temperature gradient equals the applied temperature gradient.

Because of this effect, it is essential that the induced temperature gradient rather than the applied temperature gradient be used to calculate the thermal conductivity, as is demonstrated by the data in Fig. 4. The thermal conductivity is essentially the ratio of the adiabatic rate of change of the first energy moment to the temperature gradient,

\[
\lambda = \left\langle \frac{\mathcal{E}^{\text{ad}}}{\beta_1} \right\rangle ,
\]

where the quantities that appear on the right hand side (the induced temperature gradient, the adiabatic rate of change of the first energy, and the volume) were all taken in the central half of the slit pore. The average that appears is a simple time average over the SMD trajectory. Provided that the induced temperature gradient is used, Fig. 4 shows that the resultant thermal conductivity is insensitive to the value of the variance that is used for the simulations. This is an important result that demonstrates the fundamental validity of the transition probability and the SMD algorithm.

Figure 5 compares the SMD thermal conductivity with that obtained by nonequilibrium Monte Carlo, which has been shown analytically to yield the Green–Kubo theory and to give conductivities in agreement with literature values. Using \( \sigma^2 = 0.002 \), the SMD induced temperature gradient, measured in the central half of the pore, was within 1% of the applied temperature gradient (except at \( \rho = 0.8 \) where it was 5% too low). The data in Fig. 5 clearly confirm the validity of the SMD method. In terms of computational efficiency, it appears that the SMD algorithm is more efficient than the NEMC algorithm. For the case \( \rho = 0.8 \) (\( \Delta_0 = 0.005, \sigma^2 = 0.002 \)), the standard error on the mean was 2%, and this took \( 4 \times 10^6 \) time steps, with averages being collected every ten steps. This is about a factor of 5 more efficient than the NEMC algorithm.

As mentioned in the text, constraining the reservoir perturbation to be orthogonal to the flux is very important. For example, in the case \( \rho = 0.8, T_0 = 2 \), without this constraint the thermal conductivity was \( \lambda = 5.49 \pm 0.19 \), which significantly underestimates the value obtained with the constraint, \( \lambda = 7.22 \pm 0.14 \). This supports the interpretation given in the text, namely, that real physical systems are driven at the boundaries and that the interactions with the reservoirs do not disturb the adiabatic evolution that occurs throughout the bulk of the subsystem and that determines the flux. Hence it is essential that the stochastic perturbations in the present theory that represent an idealization of the reservoirs that act throughout the subsystem be constrained to disturb minimally the adiabatic flux.

### B. Driven Brownian motion

#### 1. System details

A Brownian particle in a moving potential trap was simulated, using the same model treated in Ref. 26. The subsystem consisted of a solute atom in a bath of 1000 solvent atoms. The solute and solvent interacted via a soft-sphere potential,

\[
u_{s}(r) = \left[\sigma_{s}/r\right]^{12}.
\]

The solvent had a mass \( m_1 = 1 \), a length scale \( \sigma_1 = 0.5 \), and a potential cutoff of \( R_{\text{cut}} = 1.2 \). The solute had \( m_0 = 10 \), it in-
teracted with the solvent via $\sigma_{10}=2.25$, and $R_{\text{cut};10}=5.2$. The temperature was 3 in these units. The potential trapping the solute was a harmonic potential along the $x$-axis, oscillating along that axis,

$$U(x,t) = k[x - b(t)]^2/2,$$

(3.6)

with $k=16.81$, and $b(t)=B \sin\omega t$, with $B=2.5$. By varying the amplitude of the oscillation it was confirmed that the results were in the linear regime.

A bulk system was simulated with periodic boundary conditions. A cube of edge length 11.31 was used and the solvent density was 0.69. A spatial neighbor table with small cells was used.20

One simulation was carried out for each radial frequency $\omega$. Typically 300 oscillation cycles were simulated, using a time step of $\Delta_t=10^{-3}$ (i.e., $\approx 2 \times 10^6/\omega$ times steps, with $\omega \in [0.1,1.5]$). A cycle was divided into 20 nodes and the position and velocity of the solute were accumulated for averaging at each node. After the simulation a least-squares fit was made to these data using $\vec{x}(t) = A \sin[\omega t + \phi]$ and $\vec{v}(t) = A \omega \cos[\omega t + \phi]$, and from these fits the phase lag and the oscillation amplitude of the solute were extracted. The simulation was broken into ten blocks and ten independent fits were made in order to estimate the standard error on the mean.

2. Equations of motion

In Sec. II C it was shown that the most likely reservoir perturbation for mechanical work is $\vec{R}_{i_1} = -\beta \sigma p_{i_1}/2m_i$. Hence the first order equations of motion are

$$q_{i_1}(t + \Delta_t) = q_{i_1}(t) + \Delta_t p_{i_1}(t)/m_i,$$

(3.7)

and

$$p_{i_1}(t + \Delta_t) = p_{i_1}(t) + \Delta_t \dot{p}_{i_1}(t) = -\frac{\beta \sigma}{2m_i} p_{i_1} + \vec{R}_{i_1}(t).$$

The results reported next were obtained with second order equations of motion,

$$q_{i_1}(t + \Delta_t) = q_{i_1}(t) + \frac{\Delta_t}{2m_i} p_{i_1}(t) + \frac{\Delta_t^2}{2m_i} (1 + s_i) \times \left[ (1 - s_i) p_{i_1}(t) + \Delta_t \dot{p}_{i_1}(t) + \vec{R}_{i_1}(t) \right],$$

(3.8)

and

$$p_{i_1}(t + \Delta_t) = \frac{1}{1 + s_i} \left[ (1 - s_i) p_{i_1}(t) + \frac{\Delta_t}{2} \dot{p}_{i_1}(t) + \vec{R}_{i_1}(t) \right],$$

(3.9)

where $s_i = \beta \sigma/4m_i$. These equations result from symmetrizing the present and future adiabatic and friction forces. It is straightforward to show that this satisfies the fluctuation-dissipation theorem to quadratic order in $\sigma$. This allows one to choose a larger value of the variance than would otherwise be the case, which in turn allows a larger region of phase space to be explored in a given amount of computer time.

3. Results

Figure 6 shows the phase lag of the solute as a function of the drive frequency. The solute oscillates almost in phase with the trap at low frequencies and increasingly lags the trap as the frequency is increased, going through $\phi = \pi/2$ at approximately $\omega = 1.3$ (not shown). The results of the present SMD algorithm are compared with conventional Nosé–Hoover simulations that employ a chain thermostat.26 As discussed in Sec. II C, the most likely trajectory for this type of intensive mechanical work has the same functional form as in the equilibrium case. This perhaps explains why the Nosé–Hoover simulations, which correspond to the equilibrium Boltzmann distribution, work for this particular nonequilibrium case.

The Langevin approximation works well at low frequencies, which is the steady state regime, but increasingly underestimates the lag as the frequency is increased. The diffusion constant used in the Langevin equation, $D=0.105$, was obtained from equilibrium Nosé–Hoover chain thermostat simulations, (the mean square displacement in the absence of a trap).26 Figure 6 shows that solvent memory effects, which causes the breakdown of the Langevin approximation at higher frequencies, are well accounted for second entropy perturbation theory.26 Keeping terms to fifth order describes...
with reasonable accuracy all transient effects in the present system. The position autocorrelation function of the solute in the solvent in the absence of the perturbation was calculated using the equilibrium Nosé–Hoover chain thermostat simulations.26

The stochastic thermostat performed well. A time step of $\Delta_t = 10^{-3}$ and a variance $\sigma = 10^{-3}$ were used. The average solvent kinetic temperature was less than 1.5% greater than the reservoir temperature over the whole frequency range with these parameters. At $\omega = 0.7$, increasing both by a factor of 5 did not change any results. However, increasing the time step by a factor of 5 and leaving the variance unchanged gave a temperature 6% above the nominal one, and increasing the variance by a factor of 5 and leaving the time step unchanged decreased the response amplitude by 11%. Obviously a lower drive frequency or a smaller drive amplitude would allow a smaller variance to be used to attain the desired temperature with a reduced perturbation of the dynamics.

Figure 7 shows the ratio of the amplitude of the solute response to the amplitude of the driven trap. Interestingly enough, both simulation methods show that this is greater than one at small but nonzero frequencies. It can be seen that the response amplitude decreases with increasing frequencies. Again there is good agreement between the two simulation methods. Increasing the amplitude by a factor of 2 did not change the relative response amplitude in the Nosé–Hoover chain simulations, which confirms that the results were in the linear regime.

The second entropy theory gives the probability distribution for the solute in a moving trap as14

$$\rho(x, t|[b]) = \frac{1}{Z(t|[b])} e^{-\beta m_0(x - \bar{x}(t))^2/2} e^{-\beta \kappa (x - \bar{x}(t))^2/2}. \quad (3.10)$$

This predicts that the fluctuations about the most likely state are given by

$$\langle (x - \bar{x}(t))^2 \rangle_i = \langle x^2 \rangle_i - \langle \bar{x} \rangle_i^2 = 1/\beta m_0 \quad (3.11)$$

and

$$\langle (x - \bar{x}(t))^2 \rangle_j = \langle x^2 \rangle_j - \langle \bar{x} \rangle_j^2 = 1/\beta \kappa. \quad (3.12)$$

This result is tested in Fig. 8, which shows these fluctuations, normalized by their respective right hand sides. The SMD simulation data confirm the probability distribution and one concludes that the fluctuations in a nonequilibrium system about the most likely state have exactly the same character as the fluctuations in an equilibrium system.