Using Nonequilibrium Fluctuation Theorems to Understand and Correct Errors in Equilibrium and Nonequilibrium Simulations of Discrete Langevin Dynamics

D)
$$
1 + A. 8 + \frac{1}{2} = D. \frac{C}{B} = \frac{1}{2} + \frac{3}{4} + \frac{1}{4} = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{1}{2}
$$

where $s \rightarrow 1$ is defined by its $\sqrt{1 + \frac{1}{2}}$ dependent Hamiltonian H $f(t)$, I and $\begin{bmatrix} 1 & t & t & t \\ t & t & t & t \\ t & t & t & t \end{bmatrix}$ $\mu_{\rm B}$ is $\mu_{\rm B}$, $\mu_{\rm B}$ environment, γ friction coefficient (with dimensions of f_{α} (with dimensions of f_{α}

 $\frac{-\partial \mathcal{H}}{\partial r}$. For μ , Music $\frac{d\mathbf{W}}{dr}$, multipliers t_i , i, r, v, f, $\frac{1}{2}$ dW $\frac{1}{3}$, $\frac{1}{2}$ m $\frac{1}{3}$ I n order to simulate Langevin dynamics on a digital te simulate Langevin dynamics on a dig computer is necessary to a process \mathbb{R}^n in \mathbb{R}^n is necessary to a process \mathbb{R}^n is necessary $r_{\rm s}$ divides time into divides the into discrete steps $2 \cdot$ H \rightarrow m_1 such states m_1 such that m_2 in the schemes m_1 in m_2 in m_3 in m_4 \mathbf{t} time-Hamiltonian, the serve theorem \mathbf{H} \mathcal{A} and \mathcal{Q} and \mathcal{H} is the distribution distribution determined by H normalized by H normalized by H normalized by H \mathcal{H} is the set of \mathcal{H} is the set of \mathcal{H} is the set of \mathcal{H} is the set do the satisfy microscopic reversibility \mathbf{u}_s , \mathbf{u}_s reversibility. $\begin{array}{lllllllllllllllll} & & \text{if } \mathbb{I}_{n} & \text{if } \mathbb{I}_{n}, & \text{if } \mathbb{I}_{n} & \text{if } \math$ $M \cap N$ in \mathbb{R} , popular integration depends on \mathbb{R} integration. to $N = M - \frac{1}{2}M + M$ $\frac{1}{2}$ iii 7,[8](#page-9-3),

$$
v\left(n + \frac{1}{2}\right) = v(n) + \frac{t}{2} \frac{f(n)}{m},
$$
 (2)

$$
r(n + 1) = r(n) + \frac{1}{t} \nu \left(n + \frac{1}{2} \right),
$$
 (2)

$$
v(n + 1) = v\left(n + \frac{1}{2}\right) + \frac{t}{2} \frac{f(n + 1)}{m}.
$$
 (2)

 B enerated of the finite time step, the trajectories generated by f \mathbf{b}_s the individual \mathbf{b}_s are individual \mathbf{b}_s in faithfully dominant faithfully dominan $f_{\rm eff}$ follow $N = \frac{N}{2}$ is $\frac{N}{2}$ method. Also, the precess of $N = \frac{N}{2}$ is $\frac{N}{2}$ in $\frac{N}{2}$ in $\frac{N}{2}$ is $\frac{N}{2}$ in $\frac{N}{2}$ in $\frac{N}{2}$ is $\frac{N}{2}$ in $\frac{N}{2}$ in $\frac{N}{2}$ in $\frac{N}{2}$ is $\frac{N}{$ \mathbf{d} and \mathbf{d} is not conserved, but rather is not conserved, but \mathbf{d}_s if \mathbf{d}_s for $\frac{1}{2}$ function $\frac{1}{2}$. However, the next step to the nex velocity vertex is the integration scheme is symplectic (in the that the that the theorem is v \mathbf{J}_1 , \mathbf{q}_2 , \mathbf{q}_3 is transformation from our position from \mathbf{r}_1 $\frac{1}{2}$ and $\frac{1}{2}$ if $u = 9$), which amelion and $u = 1$ due to the finite time step. For example, and \mathbf{f}_s \mathbf{t} time-step symplectic integrator does not conserve the en- $\mathbf{A}_{\mathcal{N}}=\frac{1}{2}$ of the system Hamiltonian, \mathbf{H} and \mathbf{H} $\mathbb{E}[\mathbf{A}_\infty]$ is close to the Hamiltonian, which is close to the top to the top the top to the top the top theory is close desime Hamiltonian is not to the time step is not to the time step is not to the time step is not to the time $\frac{1}{2}$. $F = \frac{1}{2} \sum_{i=1}^n \frac{1}{i} \sum_{j=1}^n \frac{1}{j} \frac{1}{j} \frac{1}{j} \frac{1}{j} \frac{1}{j} \frac{1}{j} \frac{1}{j} \ldots$ \mathbb{R}^d Hamiltonian prevents long-term drift in the system of th $\mathrm{Hilb}_\mathbf{q}$ is during the duration of the simulation of the simulation of the simulation of the simulation. E ,所以,涉。" [1] [1] [1] [1] [1] [1] [1] \mathbf{z} , i, \mathbf{y} and \mathbf{z} , \mathbf{z} , \mathbf{z} , \mathbf{z} $\lim_{n \to \infty} \frac{1}{n}$ in $\lim_{n \to \infty} \frac{1}{n}$. Hamiltonian $\lim_{n \to \infty} \frac{1}{n}$ in $\lim_{n \to \infty} \frac{1}{n}$ c_1 in this finite-time-time-step integration scheme in the int f_{μ} for ψ , A_{μ} which is ψ , ψ , we find perturb the system \mathbb{H} is become that it becomes the such that it is a such that it is a su \mathbb{R} shadow Hamiltonian, changing the energy of the system. $T_{\rm s}$ symplectic integration and updates the position and η \mathfrak{p} , \mathfrak{p} , \mathfrak{p} , \mathfrak{p} , perfection energy energ $\mathcal{F}_{\mathbf{x}}$, $\mathcal{F}_{\mathbf{x}}$ then such that $\mathcal{F}_{\mathbf{x}}$ is the Hamiltonian. We then switch the Hamiltonian switch the Hamilton \mathbf{d}^t to the original one, and \mathbf{d}^t the energy. The network the energy of \mathbf{d}^t change in the system of the system during the system during the system of the sys due to work performed on the system by performed Φ $f_{\rm eff}$ for system and shadow Hamiltonian. We can determine the third \mathbb{Q}^k and \mathbb{Q}^k as error work [6](#page-9-6) $\frac{1}{2}$ is $\frac{1}{2}$ in $\frac{1}{2}$ in $\frac{1}{2}$ in $\frac{1}{2}$ in $\frac{1}{2}$ \mathbb{R}^n measuring the difference in the system H_1^{α} and H_2^{α} is a conomic to the form of t \mathbb{R} dow Hamiltonian. This shadow work is distinct from any \mathbb{R} protocol work applied to the system due to the system due to the system due to explicit the system of the system due to explicit the system dependent perturbations of the system Hamiltonian Hamiltonian Hamiltonian Hamiltonian Hamiltonian. Notes \mathcal{C}_1 Markov-chain Markov-chain Monte C₁ (MCMC) simulations of \mathcal{C}_1 not generate shadow work $\begin{bmatrix} 12 & 0 \end{bmatrix}$ $\begin{bmatrix} 12 & 0 \end{bmatrix}$ $\begin{bmatrix} 12 & 0 \end{bmatrix}$ because the dynamics satisfies the dynamics satisfies the dynamics satisfies $\begin{bmatrix} 1 & 0 \end{bmatrix}$ $\mathbf{x} = \mathbf{y} \mathbf{y} + \mathbf{y} \mathbf{y} = \mathbf{y} \mathbf{y}, \mathbf{y} \mathbf{y}' = \mathbf{y} \mathbf{y}$ r_1 and r_2 and r_3 and r_4 and r_4 and the theorem is r_4 and the theorem is r_4 appropriate ensure ensure is presented for a timein den Hamiltonian \mathbb{H} D is time Langevin dynamics of continuous-time Langevin dynamics of \mathbb{R}^n \mathcal{A} re estentially a combination of deterministic and stochastic an t ich dynamics, and, as a result, they suffer from a combination f t ion of problems. With a finite time step, the deterministic terministic te p and dynamics the dynamics the system into \mathbf{r}_i in form of shadow work, driving the system and system and system are system as \mathbf{r}_i \mathbb{Q} where \mathbb{Q} is the stochastic part stochastic parts of the dynamics of the dynamics of the dynamics of the dynamics \mathbb{Q} \mathbb{R} relativities back toward the equilibrium \mathfrak{g} B_1 in distribution, removing the system of A_2 from the system the system the system of A_1 in the form of heat. It follows that is defined as $\mathbb{E}_{\mathbf{z}}$ in $\mathbb{E}_{\$ $\mathbb{H}[\mathbb{F}_q \cup \mathbb{F}_q \setminus \mathbb{F}_q]$ to independent, and \mathbb{F}_q independent, a finite-

$$
\begin{array}{ccccccccc}\n\text{S} & \text{A} & \text{A} & \text{B} & \text{C} & \text{A} &
$$

 $F_e/N_{\text{H}_2\text{O}}k_\text{B}T \approx a t^4$, (7)

where the prefactor and prefactor and prefactor $a = a$ $\text{supp}(x)$ in $\text{supp}(x)$ is the caption of Fig. [2.](#page-4-0) This trend is consistent with earlier work observing the strong dependence of Metropolities on the probabilities on the set of \mathbb{R}^n $\begin{array}{ccc} 36 & 1 & A_{34}A_{33} & 1 & 1 \end{array}$ $\begin{array}{ccc} 36 & 1 & A_{34}A_{33} & 1 & 1 \end{array}$ $\begin{array}{ccc} 36 & 1 & A_{34}A_{33} & 1 & 1 \end{array}$ reductions in time small reductions in time small reductions in time small reductions in the small reductions in the small reductions in the small reductions in the small reductions i Δ rapid Δ reduce the deviations of the sampled values of the sa steady-state distribution from the distribution from the distribution of Ω (Magnetic Algorithm). $t \rightarrow \infty$ defined by the system Hamiltonian pe $(-8.4f(x))$ e $[-\beta \mathcal{H}(x)]$ $\mathcal{H}(x)$, $\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}$ \mathcal{N} is \mathcal{N} $\mathbb{E}_{\mathbf{z}} = \mathbb{E}_{\mathbf{z}} \mathbb{Q} \mathbb{W}$ in the particular perturbations. Even in the \mathbb{Q} \mathbb{R}^2 correction procedures, the above calculation procedures, the above calculation \mathbb{R}^2 4Li_1 in the theory $\mathcal{L}_{\mathbf{x}}$ of the decision from \mathbf{Q} \mathbf{W} and \mathbf{q} and \mathbf{q} \mathbb{R}^d in the continuous Langevin equation of \mathbb{R}^d . Latting \mathbb{R}^d is a model of model of model \mathbb{R}^d t_1 and a function of \mathbb{R}^n , and \mathbb{R}^n

VI. RECOVERING EQUILIBRIUM STATISTICS FROM NONEQUILIBRIUM SIMULATIONS

integrated transient fluctuation theorem (ITFT) [Eq. [\(15](#page-7-0))].

 22 to context with multiple sources of S_{u} other modified fluctuation theorems can be derived from the derived from the derived from the derived from the \mathbf{r}

 \mathbb{Z} the with an exponential average over the other than \mathbb{Z} \mathbb{P}^1 . For Ψ' \mathfrak{p} , \mathfrak{p} Sec. [VI](#page-4-1), we define a \mathfrak{p} \mathfrak{p} \mathfrak{p}

equation modified by the presence of shadow work $\begin{bmatrix} 1 & 0.1 & S \\ 1 & 0.1 & S \\ 0 &$

 EQ ([9\)](#page-4-2) P is not one of E and E


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A_n and A_n to Q_n if q_1 is the statistical statistics is Q_nt^4to \frac{1}{2} M<sub>a</sub> t^2 C<sub>1</sub>, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{42}{43},
generating an ensemble of trajectories based on the proba-
\mathcal{W}, \mathcal{A} bility associated with the Boltzmann-Weighted work over \mathcal{W}, \mathcal{A}\int_{\epsilon}^{\epsilon} is \int_{\epsilon}^{\epsilon} e^{f} \cdot e^{f} \cdot \left\{-\beta W_{\text{shad}}\right\}
```

$$
\frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}} \frac{1}{4} \prod_{j=1}^{4} \frac{1}{4} \sum_{\substack{i=1 \\ i \neq j}} \frac{1}{2} \prod_{\substack{i=1 \\ i \neq j}} \frac{1}{2}
$$

VIII. EPILOGUE

 $F=\mathrm{H} \mathbb{F}_q$ in dynamics, and \mathbb{F}_q in the finite-time-step symplec-time-symplec t integration in the $\frac{1}{2}$ shadow Hamiltonian and is $\frac{1}{2}$ in the $\frac{1}{2}$ \mathbb{P} reversible. But, as we have seen for \mathbb{P} L langevin dynamics, discretization of the dynamics leads the dynamics leads to dynamics leads to dynamics leads the dynamics leads to dynamics lead (even for a time-independent Hamiltonian) to a mixed deterministic nonegulidibrium dynamics, which is a stochastic nonpreserves the equilibrium distribution of \mathcal{Q}^{in} and $\mathcal{Q}^$ $t = \frac{1}{2}$ and $\frac{1}{2}$ Highlightonian and $\frac{1}{2}$ is not time $r_{\rm eff}$ in the measure the work, we can measure the work $r_{\rm eff}$ and $r_{\rm eff}$ and $r_{\rm eff}$ $\mathbb{P}^1_{\mathbb{P}^1_{\mathbb{P}^2_{\mathbb{P}^1_{\mathbb{$

 \mathbb{R} we say that \mathbb{R} in the same and momenta from and momenta from and momenta from and momenta from and \mathbb{R} Q V i NPT ensemble at 1 and 1 and $\frac{1}{2}$ atm and 298 K $\frac{1}{2}$ $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{8}$ $\frac{1}{2}$ M_n C₃₁ (GHMC $\frac{1}{4}$ $\frac{1}{35}$ $\frac{1}{35}$ $\frac{1}{35}$ using a time step of μ for μ for μ M_+ C_1 , $1 + \mu_1 - \mu_2$ and $1 + \mu_3 - \mu_4$ size automatically determined during \mathbf{u} and \mathbf{u} and \mathbf{u} [58](#page-10-10),59 A_1 initial $9 \,$ in $11 \div 250\,000$ steps, we \mathcal{F} is a \mathcal{F} in \mathcal{F} in \mathcal{F} and \mathcal{F} and \mathcal{F} in \mathcal{F} and \mathcal{F} is a set of \mathcal{F} in \mathcal{F} is a set of \mathcal{F} in \mathcal{F} is a set of \mathcal{F} is a set of \mathcal{F} is a set of \math $\frac{1}{2}$ iii Langevin simulation $\frac{1}{2}$ iii Langevin simulation $\frac{1}{2}$ $\frac{1}{2}$ at fixed volume using $\frac{1}{2}$ and $\frac{1}{2}$ inter $g = 1$ and $f = 11$ and $f = 11$ and $f = 4096$ u_1 and u_2 from u_3 from u_4 from u_5 from u_5 from u_6 from u_7 from u_8 from u_7 from u_8 from u_7 from u_8 from u_7 from u_8 from u_7 fro $7 \frac{c}{\log 2}$ $\frac{1}{3}$ $\frac{1}{12}$ $\frac{1}{2}$ $\frac{1}{3}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\sum_{i=1}^{2293}$ $\oint_{\mathcal{A}} h = 0, 1, ..., 12$. The largest time step that did not generate infinite i cumulative work values in 4096 time steps \mathbf{u} to \mathbf{u} ; the limit $2 + \frac{1}{2}$ for unconstrained to be 2 from unconstraint \mathbb{R} \mathbf{u} in \mathbf{u} for constraints and \mathbf{u} for \mathbf{u} for constraints. power p_0 and the state is and the state in the state of p_0 and the state in the state of p_0 $\mathbb{Z}_{3642.4}^{642.4}$, $\mathbb{Z}_{384}^{(n-0,1,\ldots,12)}$, $\mathbb{Z}_{384}^{(n-0,1,\ldots,12)}$, $\mathbb{Z}_{384}^{(n-0,1,\ldots,12)}$

T 111, 12 EQ. (6), 7 - 9 W 11.5
\n
$$
A, \frac{1}{2}, \frac{1}{3}, \frac{1}{3}, \frac{1}{3}, \frac{1}{3}, \frac{1}{4}, \frac{1}{5}, \frac{1}{5}, \frac{1}{5}
$$
\n
$$
A, \frac{1}{2}, \frac{1}{3}, \frac{1}{3}, \dots, \frac{1}{3}, \frac{1}{3},
$$

 H , $\langle \cdot \rangle_{\text{GHMC}}$ and $\langle \cdot \rangle_{\text{GHMC}}$ $\mathbf{L} \cdot \mathbf{M}$ itial configurations and momenta and momenta $\mathbf{L} \cdot \mathbf{M}$ $M = 2^n$
 $\frac{1}{2}$ $\$

$$
\delta^{2}(\mathbf{F}_{e}) = [\mathbf{a}^{f}(W_{0\rightarrow M}) + \mathbf{a}^{f}(W_{M\rightarrow 2M})
$$

\n
$$
- 2\mathbf{c}' \cdot (W_{0\rightarrow M}, W_{M\rightarrow 2M})]/(4N_{eff}), \quad (A2)
$$

\n
$$
\delta^{2}(\mathbf{F}_{e}) = \mathbf{a}^{f}(x) \mathbf{1} - \mathbf{c}' \cdot (x, y) = -\mathbf{a}^{f} \mathbf{1} - \mathbf{a}^{f} \mathbf{1} + \mathbf{a}^{f} \mathbf{1} - \mathbf{a}^{f}
$$

\n
$$
\mathbf{a}^{f}(x) \mathbf{1} - \mathbf{c}^{f} \mathbf{1} - \mathbf{a}^{f} \mathbf{1} - \mathbf{
$$

 $a_1a_2\cdots a_n$ of sequentially sampled trajectory work values. $(S \t S \t . 2.4 \t F R \t . 60.)$ $(S \t S \t . 2.4 \t F R \t . 60.)$ $(S \t S \t . 2.4 \t F R \t . 60.)$