

## Detailed Balance in Ehrenfest Mixed Quantum-Classical Dynamics

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**Abstract:** We examine the equilibrium limits of self-consistent field (Ehrenfest) mixed quantum-classical dynamics. We derive an analytical expression for the equilibrium mean energy of a multistate quantum oscillator coupled to a classical bath. We show that, at long times, for an ergodic system, the mean energy of the quantum subsystem always exceeds the temperature of the classical bath that drives it. Furthermore, the energy becomes larger as the number of states increases and diverges as the number of quantum levels approaches infinity. We verify these results by simulations.

### 1. Introduction

Mixed quantum-classical dynamics (MQCD), in which selected quantum mechanical degrees of freedom are coupled to a system of classical mechanical degrees of freedom, has proved to be a useful complement to standard classical molecular dynamics (MD) simulations. Quantum effects including electronic transitions,<sup>1,2</sup> proton tunneling, and zero-point motion<sup>3–6</sup> can be introduced within a computationally tractable classical MD framework. A critical requirement for the success of a MQCD theory is the proper treatment of the “quantum backreaction”, the altering of the classical forces due to transitions in the quantum subsystem.<sup>7–12</sup> Two widely used approaches for approximating the quantum backreaction have emerged, “surface hopping”<sup>13–15</sup> and “Ehrenfest”.<sup>16–20</sup> In both approaches, quantum transitions arise in the same way, governed by the time-dependent Schrödinger equation in which the time variation of the Hamiltonian arises from the motions of the classical particles. The methods differ only in the way the classical paths evolve. In surface hopping, the forces derive from a single quantum state, subject to sudden stochastic “hops” to different quantum states. The Ehrenfest method is a self-consistent field method; the forces governing the classical particles arise from a weighted average of quantum states. Both the surface-hopping and Ehrenfest methods allow for energy transfer between the quantum and classical subsystems such that the

total energy is conserved, and both methods have proved quite accurate in many applications.

We showed in a previous paper that, for a two-level quantum system coupled to a many-particle classical bath, the “fewest-switches” version of surface hopping<sup>13</sup> correctly obeys detailed balancing; the two-level system approaches a quantum temperature equal to the classical temperature of the bath.<sup>21</sup> This is not necessarily the case for the Ehrenfest method, as has been discussed by several authors,<sup>21–24</sup> signaling a potentially serious deficiency of the method. We previously derived a closed-form expression for the mean energy of a two-level quantum system coupled by Ehrenfest dynamics to a classical bath, showing that the quantum subsystem approaches a temperature that is finite but higher than the temperature of the classical bath to which it is coupled.<sup>21</sup> In this paper, we generalize our previous result to a quantum subsystem composed of an arbitrary number of quantum states. For the special case of equally spaced quantum levels, we are able to obtain an exact, closed-form expression for the mean energy of the quantum subsystem. This expression shows, remarkably, that in the limit of an infinite number of equally spaced levels, that is, a harmonic oscillator, the mean energy of the quantum subsystem approaches infinity no matter how low the classical temperature that drives it. The populations of each state are not equal in this limit, so the quantum subsystem does not approach infinite temperature. However, the populations decrease with increasing quantum number sufficiently slowly so that the mean energy diverges.

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## 2. Two-Level Quantum Subsystem

In a previous publication,<sup>21</sup> we derived a closed-form expression for the equilibrium mean energy of a two-level quantum subsystem coupled to an infinite number of classical particles via the Ehrenfest self-consistent field approximation. We recast the amplitudes  $c_\alpha$  and  $c_\beta$  of quantum levels  $\alpha$  and  $\beta$  into two new variables

$$X = |c_\beta|^2 = 1 - |c_\alpha|^2 \quad (1a)$$

and

$$Y = c_\alpha^* c_\beta + c_\beta^* c_\alpha \quad (1b)$$

The variables  $X$  and  $Y$  can be shown to behave as effective classical variables.<sup>25</sup> We derived a classical Liouville equation for the probability distribution  $f(\mathbf{q}, \mathbf{p}, X, Y)$  of the positions  $\mathbf{q}$  and momenta  $\mathbf{p}$  of the classical particles and the variables  $X$  and  $Y$ . We then obtained the steady-state solution of the Liouville equation, which produced the following simple expression for the equilibrium mean energy of the quantum subsystem in terms of the temperature,  $T$ , of the classical bath:

$$\bar{E} = \langle |c_\beta|^2 \rangle \epsilon_\beta = k_B T - \frac{\epsilon_\beta \exp[-\epsilon_\beta/k_B T]}{1 - \exp[-\epsilon_\beta/k_B T]} \quad (2)$$

where the energy of the lower quantum level  $\alpha$  is taken to be zero,  $\epsilon_\beta$  is the energy of the upper level  $\beta$ , and  $k_B$  is Boltzmann's constant. It can be shown with some algebra that the mean energy of the quantum subsystem produced by Ehrenfest dynamics, as given by eq 2, is always greater than the desired Boltzmann energy

$$\bar{E}_{\text{BOLTZ}} = \frac{\epsilon_\beta \exp[-\epsilon_\beta/k_B T]}{1 + \exp[-\epsilon_\beta/k_B T]} \quad (3)$$

## 3. Three-Level Quantum Subsystem

We first generalize this result to a three-level quantum subsystem and, later, to an  $N$ -level system. We follow the same procedure as above. The three-level quantum subsystem is described in an adiabatic basis. The wave functions  $\alpha_q$ ,  $\beta_q$ , and  $\gamma_q$  are the eigenfunctions of the quantum Hamiltonian for fixed classical positions  $\mathbf{q}$

$$\mathcal{H}_q \alpha_q = \epsilon_\alpha(\mathbf{q}) \alpha_q \quad (4a)$$

$$\mathcal{H}_q \beta_q = \epsilon_\beta(\mathbf{q}) \beta_q \quad (4b)$$

$$\mathcal{H}_q \gamma_q = \epsilon_\gamma(\mathbf{q}) \gamma_q \quad (4c)$$

The subscript  $q$  indicates that the quantum Hamiltonian and its eigenfunctions depend parametrically on the classical positions  $\mathbf{q}$ . The eigenenergies  $\epsilon_\alpha(\mathbf{q})$ ,  $\epsilon_\beta(\mathbf{q})$ , and  $\epsilon_\gamma(\mathbf{q})$ , in general, are also functions of  $\mathbf{q}$ ; they are the adiabatic potential energy surfaces for states  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively. We express the wave function of the quantum subsystem at any time  $t$  as a linear combination of  $\alpha_q$ ,  $\beta_q$ , and  $\gamma_q$

$$\psi(t) = c_\alpha(t) \alpha_q + c_\beta(t) \beta_q + c_\gamma(t) \gamma_q \quad (5)$$

where  $c_\alpha(t)$ ,  $c_\beta(t)$ , and  $c_\gamma(t)$  are the complex-valued expansion

coefficients. Substituting eq 5 into the time-dependent Schrödinger equation gives a set of coupled differential equations for the time-varying amplitudes  $c_\alpha(t)$ ,  $c_\beta(t)$ , and  $c_\gamma(t)$ :

$$\dot{c}_\alpha = -\frac{i}{\hbar} \epsilon_\alpha c_\alpha - \dot{\mathbf{q}} \cdot \mathbf{d}_{\alpha\beta} c_\beta + \dot{\mathbf{q}} \cdot \mathbf{d}_{\gamma\alpha} c_\gamma \quad (6a)$$

$$\dot{c}_\beta = -\frac{i}{\hbar} \epsilon_\beta c_\beta + \dot{\mathbf{q}} \cdot \mathbf{d}_{\alpha\beta} c_\alpha - \dot{\mathbf{q}} \cdot \mathbf{d}_{\beta\gamma} c_\gamma \quad (6b)$$

$$\dot{c}_\gamma = -\frac{i}{\hbar} \epsilon_\gamma c_\gamma - \dot{\mathbf{q}} \cdot \mathbf{d}_{\gamma\alpha} c_\alpha + \dot{\mathbf{q}} \cdot \mathbf{d}_{\beta\gamma} c_\beta \quad (6c)$$

where we have assumed, for simplicity of notation, that the adiabatic wave functions  $\alpha_q$ ,  $\beta_q$ , and  $\gamma_q$  are real-valued. The nonadiabatic coupling vector  $\mathbf{d}_{\alpha\beta}$  is given by

$$\mathbf{d}_{\alpha\beta} = \langle \alpha_q | \nabla_q \beta_q \rangle \quad (7)$$

Couplings between the other states are defined similarly. Note that, because we have chosen the adiabatic representation, there is no potential energy term coupling the quantum levels. Since the Ehrenfest method is invariant to choice of representation,<sup>26</sup> the results we derive here apply for any valid representation. From eq 6, we obtain the time derivatives of the populations.

$$\frac{d}{dt} |c_\alpha|^2 = -\dot{\mathbf{q}} \cdot \mathbf{d}_{\alpha\beta} (c_\alpha^* c_\beta + c_\beta^* c_\alpha) + \dot{\mathbf{q}} \cdot \mathbf{d}_{\gamma\alpha} (c_\alpha^* c_\gamma + c_\gamma^* c_\alpha) \quad (8a)$$

$$\frac{d}{dt} |c_\beta|^2 = \dot{\mathbf{q}} \cdot \mathbf{d}_{\alpha\beta} (c_\alpha^* c_\beta + c_\beta^* c_\alpha) - \dot{\mathbf{q}} \cdot \mathbf{d}_{\beta\gamma} (c_\beta^* c_\gamma + c_\gamma^* c_\beta) \quad (8b)$$

$$\frac{d}{dt} |c_\gamma|^2 = \dot{\mathbf{q}} \cdot \mathbf{d}_{\beta\gamma} (c_\beta^* c_\gamma + c_\gamma^* c_\beta) - \dot{\mathbf{q}} \cdot \mathbf{d}_{\gamma\alpha} (c_\alpha^* c_\gamma + c_\gamma^* c_\alpha) \quad (8c)$$

Summing all parts of eq 8 demonstrates conservation of norm. We define four independent effective classical phase space variables for the quantum subsystem,  $U$ ,  $S$ ,  $W$ , and  $X$ , in terms of the quantum amplitudes:

$$U = |c_\beta|^2 \quad (9)$$

$$S = |c_\gamma|^2 \quad (10)$$

$$W = c_\beta^* c_\gamma + c_\gamma^* c_\beta \quad (11)$$

$$X = c_\beta^* c_\alpha + c_\alpha^* c_\beta \quad (12)$$

The variables  $U$ ,  $S$ ,  $W$ , and  $X$  are the independent variables required to characterize a three-state system. Whereas the three complex-valued amplitudes introduce six variables, two are not independent. The quantity  $|c_\alpha|^2$  is determined by conservation of norm, and the variable

$$Y = c_\gamma^* c_\alpha + c_\alpha^* c_\gamma \quad (13)$$

can be expressed as follows in terms of the independent variables:

$$Y = \frac{\pm \sqrt{4US - W^2} \sqrt{4U - 4U^2 - 4US - X^2 + WX}}{2U} \quad (14)$$

From eqs 8–12, we obtain equations for the time derivatives of the four effective classical variables  $U$ ,  $S$ ,  $W$ , and  $X$ :

$$\dot{U} = -\dot{\mathbf{q}} \cdot \mathbf{d}_{\beta\gamma} W + \dot{\mathbf{q}} \cdot \mathbf{d}_{\alpha\beta} X \quad (15)$$

$$\dot{S} = \dot{\mathbf{q}} \cdot \mathbf{d}_{\beta\gamma} W - \dot{\mathbf{q}} \cdot \mathbf{d}_{\gamma\alpha} Y \quad (16)$$

$$\dot{W} = 2(U - S)\dot{\mathbf{q}} \cdot \mathbf{d}_{\beta\gamma} - \dot{\mathbf{q}} \cdot \mathbf{d}_{\gamma\alpha} X + \dot{\mathbf{q}} \cdot \mathbf{d}_{\alpha\beta} Y \pm \frac{(\epsilon_\gamma - \epsilon_\beta)}{\hbar} \sqrt{4US - W^2} \quad (17)$$

$$\dot{X} = 2(1 - 2U - S)\dot{\mathbf{q}} \cdot \mathbf{d}_{\alpha\beta} + \dot{\mathbf{q}} \cdot \mathbf{d}_{\gamma\alpha} W - \dot{\mathbf{q}} \cdot \mathbf{d}_{\beta\gamma} Y \pm \frac{(\epsilon_\alpha - \epsilon_\beta)}{\hbar} \sqrt{4U - 4U^2 - 4US - X^2} \quad (18)$$

The two separate branches ( $\pm$ ) in eqs 17 and 18 can be treated separately and, thereby, pose no mathematical difficulty. As the quantum subsystem evolves according to the time-dependent Schrödinger equation, the classical subsystem evolves self-consistently according to Hamilton's equations of motion. As for the two-level case, the phase space variables of the classical subsystem are  $(\mathbf{q}, \mathbf{p})$  where  $\mathbf{q}$  and  $\mathbf{p}$  are the positions and momenta, respectively, of the  $N_c$  number of classical particles. For simplicity of notation, we assume that the classical variables have been transformed into a frame in which the quantum system is coupled to only a single component of momentum,  $p_1$ . As shown elsewhere,<sup>27</sup> using mass-weighted coordinates, this can be achieved for any pair of quantum levels. We assume further that all of the nonadiabatic couplings are in the same direction. The latter is not true in general, but since detailed balance is a statement about the forward and backward transition rates between a pair of quantum states, this simplification cannot affect the final results. As a result of these simplifying assumptions, the dot products can be replaced by scalar multiplications in eqs 15–18. The backreaction of the quantum subsystem on the classical subsystem is incorporated as the Hellmann–Feynman force, which acts only on classical momentum 1.

$$\begin{aligned} \dot{p}_1 &= -\frac{\partial V(\mathbf{q})}{\partial q_1} - \frac{\partial}{\partial q_1} \langle \psi(t) | H_q | \psi(t) \rangle \\ &= -\frac{\partial V(\mathbf{q})}{\partial q_1} - (\epsilon_\gamma - \epsilon_\beta) d_{\beta\gamma} W - (\epsilon_\beta - \epsilon_\alpha) d_{\alpha\beta} X - \\ &\quad (\epsilon_\alpha - \epsilon_\gamma) d_{\gamma\alpha} Y \quad (19) \end{aligned}$$

Now equipped with the time derivatives of the phase space variables (quantum and classical), we proceed to derive the probability distribution function  $f(\mathbf{q}, \mathbf{p}, U, S, W, X)$ , which obeys the Liouville equation (see McQuarrie<sup>28</sup>)

$$\begin{aligned} \frac{\partial f}{\partial t} &= \sum_{i=1}^{N_c} \left[ \frac{p_i}{m} \frac{\partial f}{\partial q_i} - \frac{\partial V}{\partial q_i} \frac{\partial f}{\partial p_i} \right] + \frac{\partial(f\dot{U})}{\partial U} + \frac{\partial(f\dot{S})}{\partial S} + \frac{\partial(f\dot{W})}{\partial W} + \\ &\quad \frac{\partial(f\dot{X})}{\partial X} + \frac{\partial f}{\partial p_1} [-(\epsilon_\gamma - \epsilon_\beta) d_{\beta\gamma} W - (\epsilon_\beta - \epsilon_\alpha) d_{\alpha\beta} X - \\ &\quad (\epsilon_\alpha - \epsilon_\gamma) d_{\gamma\alpha} Y] = 0 \quad (20) \end{aligned}$$

The function  $f(\mathbf{q}, \mathbf{p}, U, S, W, X)$  that satisfies eq 20 is

$$f(\mathbf{q}, \mathbf{p}, U, S, W, X) = A e^{-V(\mathbf{q})/k_B T} \prod_{i=1}^{N_c} e^{-p_i^2/2mk_B T} g(U, S, W, X) \quad (21)$$

where  $A$  is a normalization constant and

$$\begin{aligned} g(U, S, W, X) &= \frac{1}{\pi^2} (4US - W^2)^{-1/2} (4U - 4U^2 - \\ &\quad 4US - X^2)^{-1/2} \exp\left[-\frac{U(\epsilon_\beta - \epsilon_\alpha)}{k_B T}\right] \\ &\quad \exp\left[-\frac{S(\epsilon_\gamma - \epsilon_\alpha)}{k_B T}\right] \exp\left(-\frac{\epsilon_\alpha}{k_B T}\right) \\ &= \frac{1}{\pi^2} (4US - W^2)^{-1/2} (4U - 4U^2 - \\ &\quad 4US - X^2)^{-1/2} \exp\left[-\left(\sum_{i=\alpha,\beta,\gamma} |c_i|^2 \epsilon_i\right)/k_B T\right] \quad (22) \end{aligned}$$

Equation 22 is the probability distribution function which determines any average properties of the three-state quantum subsystem. Because we have carried out the derivation in the adiabatic representation in which the Hamiltonian is diagonal, the energy of the quantum subsystem depends only on the probabilities  $|c_\alpha|^2$ ,  $|c_\beta|^2$ , and  $|c_\gamma|^2$ . We can then integrate eq 22 over  $dW$  and  $dX$  to obtain the un-normalized probability distribution in variables  $U$  and  $S$

$$\begin{aligned} g_{U,S}(U, S) &= \int_{W=-\sqrt{4US}}^{+\sqrt{4US}} \int_{X=-\sqrt{4U-4U^2-4US}}^{+\sqrt{4U-4U^2-4US}} g(U, S, W, X) dW dX \\ &= \exp\left[-\frac{U(\epsilon_\beta - \epsilon_\alpha)}{k_B T}\right] \exp\left[-\frac{S(\epsilon_\gamma - \epsilon_\alpha)}{k_B T}\right] \\ &\quad \exp\left(-\frac{\epsilon_\alpha}{k_B T}\right) = \exp\left(-\frac{1}{k_B T} \sum_{i=\alpha,\beta,\gamma} |c_i|^2 \epsilon_i\right) \quad (23) \end{aligned}$$

The probability distribution function  $g_{U,S}(U, S)$  is a function of only two independent variables,  $U$  and  $S$ , that is,  $|c_\beta|^2$  and  $|c_\gamma|^2$ , since the population of the ground state  $|c_\alpha|^2$  can be expressed in terms of the other two populations in accordance with conservation of norm. The simple product form of eq 23 appears deceptively simple. We note that the state populations are not independent as a simple product might suggest but are correlated because of the constraints that  $0 < |c_i|^2 < 1$  for each state  $i$ , and the sum over all states of  $|c_i|^2$  is unity.

#### 4. N-Level Quantum Subsystem

It is straightforward to generalize eq 23 to obtain the un-normalized probability distribution for an arbitrary number of quantum levels,  $N$ :

$$g_{2,3,\dots,N}(|c_2|^2, |c_3|^2, \dots, |c_N|^2) = \exp\left(-\frac{1}{k_B T} \sum_{i=1}^N |c_i|^2 \epsilon_i\right) \quad (24)$$

with the constraints  $0 < |c_i|^2 < 1$  for each state  $i$ , and the sum over all states of  $|c_i|^2$  is unity. As for the three-level

case, the probability distribution functions are correlated because of the constraint of conservation of norm.

We now derive the mean energy of an  $N$ -state quantum subsystem, using eq 24 for the probability distribution of the populations:

$$\bar{E} = \left\{ \int_0^1 d|c_2|^2 \int_0^{1-|c_2|^2} d|c_3|^2 \int_0^{1-|c_2|^2-|c_3|^2} d|c_4|^2 \dots \right. \\ \left. \int_0^{1-\sum_{i=2}^{N-1}|c_i|^2} d|c_N|^2 \left( \sum_{i=2}^N \epsilon_i |c_i|^2 \right) \exp \left( \frac{-1}{k_B T} \sum_{i=2}^N \epsilon_i |c_i|^2 \right) \right\} / \\ \left\{ \int_0^1 d|c_2|^2 \int_0^{1-|c_2|^2} d|c_3|^2 \int_0^{1-|c_2|^2-|c_3|^2} d|c_4|^2 \dots \right. \\ \left. \int_0^{1-\sum_{i=2}^{N-1}|c_i|^2} d|c_N|^2 \exp \left( \frac{-1}{k_B T} \sum_{i=2}^N \epsilon_i |c_i|^2 \right) \right\} \quad (25)$$

The ground-state energy  $\epsilon_1$  is assumed to be zero for convenience. The integrations limits in eq 25 result from conservation of norm; that is, the constraint that the sum of all probabilities be unity. Equation 25 is the basic result of this paper. The equilibrium mean energy of the quantum subsystem by the Ehrenfest method depends only on the energies of the quantum levels and is independent of the coupling strength. It is also clearly not a Boltzmann distribution, as shown below.

In the special case that the energy levels of the quantum subsystem are nondegenerate and equally spaced, eq 25 can be integrated to obtain a closed-form expression for the mean energy. Assume there are  $N$  quantum states with energies  $0, \epsilon, 2\epsilon, \dots, (N-1)\epsilon$ . The integration of eq 25 gives the simple result

$$\bar{E} = \frac{(N-1)[1 + \epsilon/k_B T - \exp(\epsilon/k_B T)]k_B T}{1 - \exp(\epsilon/k_B T)} \quad (26)$$

Note that the mean energy is proportional to  $N-1$ , the number of quantum states minus 1. Thus, for an infinite number of states, that is, for the harmonic oscillator, the equilibrium mean energy of the quantum subsystem is infinite at any finite temperature of the classical bath.

## 5. Simulations

To verify the derived expression for the Ehrenfest mean energy of an  $N$ -level system with equal energy spacing, eq 26, we have carried out numerical simulations. The classical subsystem is represented by a linear chain of  $N_c$  particles, coupled to each other by anharmonic, nearest-neighbor potentials given by

$$V(\mathbf{q}) = \sum_{k=1}^{N_c} V_M(q_k - q_{k+1}) \quad (27)$$

where

$$V_M(q) = V_0(a^2 q^2 - a^3 q^3 + 0.58a^4 q^4) \quad (28)$$

and  $q_{N_c+1}$  is a fixed position. Anharmonic interactions are

required to achieve ergodicity, that is, to ensure that the system achieves a true equilibrium independent of the classical and quantum initial conditions. This was verified numerically. The quantum subsystem is an  $N$ -level system coupled to atom 1 of the classical chain. The assumption that the quantum subsystem is coupled only to the first atom of the chain is for convenience only; it does not affect any of the conclusions. The quantum energy levels and non-adiabatic couplings are taken to be independent of  $\mathbf{q}$ . The number of classical atoms in the chain was typically chosen to be 20. A Langevin friction constant  $\gamma$  and white random force  $F(t)$  were imposed on atom number  $N_c$  of the chain, the one most distant from the quantum subsystem, to ensure that the classical subsystem maintained the correct canonical ensemble equilibrium.  $F(t)$  is a Gaussian random variable of width given by<sup>29</sup>

$$\sigma = (2\gamma m k_B T \delta^{-1})^{1/2} \quad (29)$$

where  $\delta$  is the time step of the integration. The parameters in eqs 28 and 29 were chosen to be the same as those in a previous publication,<sup>21</sup>  $V_0 = 175$  kJ/mol,  $a = 4.0$  Å<sup>-1</sup>,  $\gamma = 10^{14}$  s<sup>-1</sup>, and  $m = 12$  amu. The classical equations of motion were integrated using a modified Beeman algorithm.<sup>29,30</sup> The quantum equations of motion, describing the time evolution of the complex expansion coefficients of the wave function  $\psi$

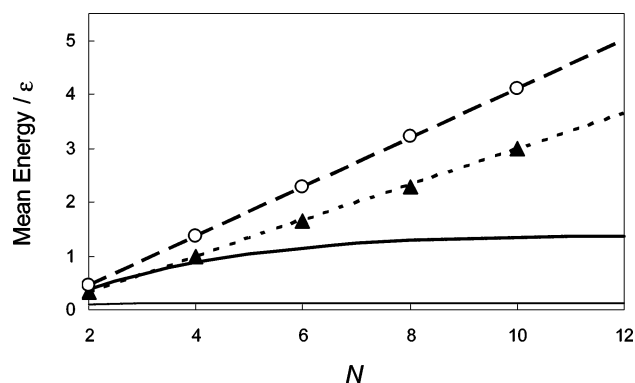
$$i\hbar \dot{c}_k = c_k \epsilon_k - i\hbar \sum_{j=1}^N \mathbf{\hat{R}} \cdot \mathbf{d}_{kj} \quad (30)$$

were integrated using the fourth-order Runge Kutta algorithm.<sup>31</sup> In our one-dimensional linear chain model, the term  $\mathbf{\hat{R}} \cdot \mathbf{d}_{kj}$  is replaced by  $p_1 d_{kj}/m$  as discussed earlier. The nonadiabatic couplings  $d_{kj}$  between quantum states  $k$  and  $j$  are given by the expression

$$d_{kj} = \frac{-\epsilon^2 \sqrt{\frac{m_H}{2\hbar^2 \epsilon}} (\sqrt{j} \delta_{k-1,j} + \sqrt{j-1} \delta_{k-1,j-2})}{\epsilon_j - \epsilon_k} \quad j \neq k; j = 1, \dots, N; k = 1, \dots, N \\ d_{kk} = 0 \quad (31)$$

In the above equation,  $\delta_{k,j}$  is the Kronecker delta. The energy gap  $\epsilon$  between adjacent levels was chosen to be 35.9 kJ/mol, and  $m_H$  was 1 amu. Ehrenfest simulations were performed for a number of quantum states,  $N = 2, 4, 6, 8$ , and 10, and for  $\epsilon/k_B T$  ranging from 0.54 (high temperature) to 2.16 (low temperature). The equilibrium averages of the Ehrenfest simulations were obtained from an ensemble of 20 trajectories, each typically 50 ps in length, with a time step  $\leq 0.005$  fs. The initial 20 ps was neglected in the averages to remove any dependence on initial conditions. The same equilibrium populations were obtained whether the quantum system started initially in any pure state or in a linear combination of quantum states, confirming that the system is indeed ergodic and that the averages correspond to true equilibrium averages, within statistical uncertainties. For low temperatures ( $\epsilon/k_B T > 2$ ) and large  $N$  values ( $N >$





**Figure 1.** Mean energy of a quantum oscillator with equally spaced energy levels, as a function of the number of quantum states,  $N$ . The dashed lines are the mean energies obtained by the Ehrenfest method, from eq 26, for  $\epsilon/k_B T = 0.54$  (---) and  $\epsilon/k_B T = 2.16$  (- - -). The circles and triangles are the Ehrenfest mean energies obtained from simulations for  $\epsilon/k_B T = 0.54$  and 2.16, respectively, confirming the validity of eq 26. Note that the Ehrenfest mean energy does not converge with increasing  $N$ . The mean Boltzmann energy as a function of  $N$  is shown for comparison for  $\epsilon/k_B T = 0.54$  (—; heavy line) and  $\epsilon/k_B T = 2.15$  (—; light line).

6), the length of each trajectory was in the 200–600 ps range, with the initial 100–400 ps neglected, since a longer time was required to achieve equilibrium.

## 6. Results

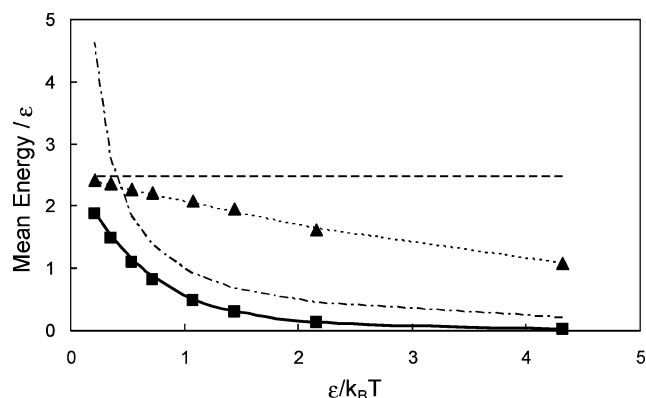
Figure 1 shows the mean energy of an  $N$ -level quantum system, with equally spaced energy levels, as derived for the Ehrenfest method, eq 26. Also shown are simulation results for  $N$  ranging from 2 to 10 and for  $\epsilon/k_B T = 0.54$  and 2.16. The simulations are in full agreement, within statistical uncertainties, with eq 26. As shown in Figure 1, the Ehrenfest result differs substantially from the desired Boltzmann distribution for an  $N$ -state quantum system

$$\bar{E}_{\text{BOLTZ}} = \frac{\sum_{i=1}^N \epsilon_i e^{-\epsilon_i/k_B T}}{\sum_{i=1}^N e^{-\epsilon_i/k_B T}} \quad (32)$$

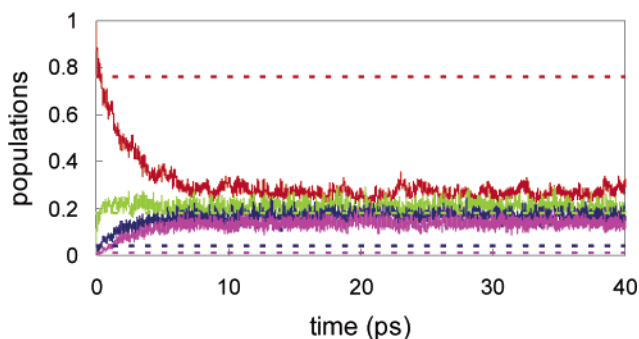
The Ehrenfest mean energy does not converge as  $N$  increases, in contrast to the Boltzmann mean energy, which closely approaches its asymptotic limit by  $N = 10$  for the parameters of Figure 1.

$$\bar{E}_{\text{BOLTZ},\infty} = \frac{\epsilon \exp(-\epsilon/k_B T)}{1 - \exp(-\epsilon/k_B T)} \quad (33)$$

The Ehrenfest mean energy also deviates from the classical expression for the mean energy of a simple harmonic oscillator,  $\bar{E}_{\text{CL}} = k_B T$ . In the limit, as  $N \rightarrow \infty$ , it is clear that, at any nonzero temperature, no matter how low, the mean energy of the Ehrenfest quantum subsystem diverges,  $\bar{E} \rightarrow \infty$ , as shown in Figure 1. This is a nonphysical result.



**Figure 2.** Mean energy of the quantum oscillator with six equally spaced energy levels as a function of inverse temperature. Triangles are the mean energies obtained by the Ehrenfest simulations. The dotted line is the analytical expression, eq 26, which agrees with the Ehrenfest simulations within statistical uncertainties. The horizontal dashed line is the mean energy at infinite temperature, i.e., when all six states are equally populated. The dash-dot shows the classical mean energy of a harmonic oscillator,  $k_B T$ . The solid curve shows the energy obtained from a Boltzmann distribution of populations for the six-level system. Squares are the results of fewest-switches surface-hopping simulations, as described elsewhere,<sup>21</sup> showing that surface hopping does achieve the correct Boltzmann equilibrium limit for the quantum subsystem.



**Figure 3.** Ensemble averaged populations as a function of time for a quantum oscillator with six equally spaced energy levels, from an Ehrenfest simulation. The simulation was carried out at  $\epsilon/k_B T = 1.44$ . The quantum subsystem was started in the ground state ( $n = 0$ ). However, the final steady-state populations do not depend on the initial state. Red, green, blue, and magenta correspond to  $n = 0, 1, 2$ , and 3, respectively. The horizontal lines show the Boltzmann populations at  $\epsilon/k_B T = 1.44$ . Only the first four levels are shown for clarity.

Figure 2 shows the mean energy of the quantum subsystem, for number of quantum levels  $N = 6$ , as a function of the unitless energy  $\epsilon/k_B T$ , that is, as a function of inverse temperature. As shown in Figure 2, the closed-form expression for the Ehrenfest mean energy, eq 26, is further verified by the simulations. The Ehrenfest mean energy is again seen to deviate substantially from both the quantum and classical Boltzmann mean energies. For comparison, the results of fewest-switches surface-hopping simulations, carried out by the procedure of a previous reference,<sup>21</sup> are also shown in

Figure 2. The surface-hopping results agree with the quantum Boltzmann results within statistical uncertainty. This offers additional verification of our previous demonstration that fewest-switches surface hopping satisfies detailed balance rigorously.<sup>21</sup>

Figure 3 shows an Ehrenfest simulation of the time evolution of the quantum state populations for a six-state quantum subsystem of equally spaced levels (only the four lowest-energy levels are shown), with 50 trajectories in the ensemble. It can be seen from Figure 3 that the Ehrenfest state populations, while not equal, are relatively close in magnitude, in contrast to the Boltzmann populations (horizontal dashed lines).

## 7. Conclusions

We have analyzed the long-time, equilibrium limit of the Ehrenfest MQCD method using a Liouville-like equation for the time evolution of the distribution function of the phase space variables. We find that the Ehrenfest method fails to achieve the correct long-time, equilibrium state; the quantum subsystem does not approach the same temperature as the classical bath that drives it. Rather, the populations of quantum levels are non-Boltzmann, and the mean energy of the quantum subsystem is too high. For the particular case of a quantum oscillator with  $N$  equally spaced levels in contact with a bath of an infinite number of classical particles, we have derived a simple closed-form analytical expression for the equilibrium mean energy of the quantum subsystem. We have verified this expression via simulations. The equilibrium Ehrenfest mean energy can be significantly higher than that given by the Boltzmann distribution of populations and nonphysically diverges with increasing  $N$ . The quantum subsystem does not approach infinite temperature in this limit; the level populations decrease with increasing energy, but do so sufficiently slowly so that the mean energy diverges.

The failure of the Ehrenfest method to achieve the correct thermal equilibrium is a result of the fact that the squares of the quantum amplitudes,  $|c_i|^2$ , which are the phase space variables for the quantum subsystem, are continuous, classical-like variables. Thus, the expectation value of an observable requires integration over  $d|c_i|^2$ , rather than a discrete sum over  $i$ , that is, over the diagonal elements of the density matrix. As the number of states  $N$  increases, the number of integration variables  $d|c_i|^2$  in the Ehrenfest theory increases proportionally, whereas the correct quantum result remains a sum over a single variable  $i$ . The consequence of this is that the effective volume of phase space corresponding to a particular energy  $E$  increases nonphysically with increasing  $E$ , giving rise to a higher average energy than the correct quantum Boltzmann result.

Failure of Ehrenfest MQCD to achieve the correct equilibrium state may seriously limit its applicability. Certainly, this prohibits its use to compute equilibrium properties. In addition, applications of the Ehrenfest method to study the rate of approach to equilibrium, such as energy relaxation, solvent reorganization, or nonradiative decay, must be carried out with caution. More generally, detailed balance relates

the equilibrium populations of two states to the ratio of forward and backward rates. If detailed balance is not satisfied, then at least one of the rates must be in error, possibly affecting even short time dynamics. As demonstrated previously,<sup>21</sup> the alternative, widely used MQCD method, fewest-switches surface hopping, does not suffer from this deficiency; at long times, the quantum and classical subsystems rigorously approach the same temperature.

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