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Eric M. Heatwole and Oleg V. Prezhdo

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Eric M. Heatwole and Oleg V. Prezhdo[a)]

Department of Chemistry, University of Washington, Seattle, Washington 98195-1700

Starting with a quantum Langevin equation describing in the Heisenberg representation a quantum system coupled to a quantum bath, the Markov approximation and, further, the closure approximation are applied to derive a semiclassical Langevin equation for the second-order quantized Hamilton dynamics (QHD) coupled to a classical bath. The expectation values of the system operators are decomposed into products of the first and second moments of the position and momentum operators that incorporate zero-point energy and moderate tunneling effects. The random force and friction as well as the system-bath coupling are decomposed to the lowest classical level. The resulting Langevin equation describing QHD-2 coupled to classical bath is analyzed and applied to free particle, harmonic oscillator, and the Morse potential representing the OH stretch of the SPC-flexible water model. © *2005 American Institute of Physics.*
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I. INTRODUCTION

Many chemical processes are well described by classical mechanics. Still, numerous examples can be found, including gas phase,[1–3] solution,[4–9] polymer,[10–12] surface,[13–18] and biochemistry,[19–22] where quantum features are clearly present or even dominate chemical phenomena. This, in combination with the fact that quantum mechanics is prohibitively expensive for the description of the majority of chemical systems, provides a strong motivation for the development of efficient semiclassical approaches that capture the essential quantum effects. Much of the recent emphasis is placed on time-dependent approximations that are suitable for modeling of the time-resolved processes observed and studied experimentally with laser techniques.

The current paper focuses on the quantized Hamilton dynamics (QHD) approach[23–32] that extends classical mechanics by addition of higher-order variables that capture quantum effects. QHD is based on the Heisenberg representation of quantum mechanics and evolves relevant observables directly, bypassing wave function or density matrix needed for a general description. Approximations are developed by closures representing higher-order variables with products of lower-order variables. The first-order QHD for the expectation values of the position and momentum operators is equivalent to the classical Hamilton dynamics. Higher-order QHDs give systems of coupled first-order equations, which are generally linear and similar to the Hamilton mechanics. The QHD equations have been derived for the observable expectation values of interest to the problem at hand, including the position and momentum operators describing the location of the particle tunneling through a barrier[23,25,26] and quantum interference,[28] kinetic and harmonic energy operators capturing zero-point energy (ZPE) effects,[23,25,26] position and energy of a heavier particle interacting with a lighter system described fully quantum

mechanically,[24] population inversion,[30] coherence transfer,[32] and state-specific coordinate.[32] Quantum systems that are exactly solvable by Lie-algebraic techniques,[33,34] such as the harmonic oscillator or spin systems, do not require a closure and are naturally represented with a finite number of operators. The well-known equations of motion for the frozen and thawed Gaussians[35–39] appear as special cases of QHD.[27]

It is often desirable to address both dynamical and statistical mechanical aspects of a problem at the same time. The transient signals observed in time-resolved laser experiments are Boltzmann averaged over initial conditions. Assuming ergodicity, dynamical trajectories of systems coupled to heat bath are customarily used in classical mechanics to sample canonical ensembles. Under linear response, dynamical fluctuations in equilibrium are related to nonequilibrium relaxation coefficients. It would be extremely valuable to establish similar relationships within the extended phase space of the QHD formalism, which provides a hierarchy of approximations to quantum dynamics. The goal, however, is more complicated that it may appear at first.

The relationship between statistical and time averages in quantum mechanics is more complex than in classical mechanics. The time evolution of a wave function or a density matrix covers more states that are needed to define a quantum statistical sum. States within a volume element on the order of $\hbar$ together give a contribution to the quantum statistical sum. The volume reduces to a point in the classical phase space, where every state accessible by a trajectory contributes to the statistical sum. The extended phase space of QHD cannot be treated as the classical phase space.

The difficulty of developing a semiclassical approximation with a classical-like relationship between statistical and time averagings can be seen in the path-integral formulation

a)Electronic mail: prezhdo@u.washington.edu

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of quantum mechanics.[40] The expressions for the statistical and time-evolution operators are similar in the mathematical form but have very different physical interpretations. Time in the path-integral quantum dynamics is the usual real time. Time in the statistical mechanical path integrals is imaginary and has the meaning of inverse temperature. The real and imaginary time path-integrals are related by analytic continuation,[41] which is not one to one and requires further postulates, such as the maximum entropy principle.[42] The dynamical and semiclassical approximations based on path integrals are also similar in formal structure, but different in physical content.[40,43–45] The same is true for the Gaussian approaches. The Gaussian Feynman–Hibbs statistical mechanics[46,47] resembles thawed Gaussians,[35,38] however, the parameters of the statistical and dynamical Gaussians have different meanings. While statistical ensembles are regularly used as initial conditions for dynamics at quantum, semiclassical and classical levels, quantum and semiclassical dynamics typically are not used for constructing statistical averages, in contrast with classical dynamics, which is routinely used for this purpose.

The approach described below extends the dynamical QHD theory for the description of statistical averages. Starting from a quantum Langevin equation, a semiclassical Langevin equation is derived by closure in both system variables and system-bath coupling. The focus is on a low-order QHD approximation, where the system is treated by QHD-2, while the bath is simplified to the classical level. The approximation avoids quantum treatment of noise and maps the semiclassical Langevin equation onto a classical Langevin equation in a double-dimensional space. The properties of QHD-2 coupled to classical bath are illustrated with free particle, harmonic oscillator, and a Morse oscillator representing the OH stretch of water.

II. THEORY

Consider the quantum Langevin equation for a system operator Y

$$\frac{dY}{dt} = \frac{i}{\hbar}[H_{\text{sys}}, Y] - \frac{i}{2\hbar}$$
$$\times \left[F(t) - \int_{t_0}^{t} \frac{dQ(t')}{dt'} f(t-t')dt', [Q(t), Y(t)] \right]_+, \quad (1)$$

where $[A, B]_+ = AB + BA$ is the anticommutator. The system is coupled to the bath through the system coordinate Q. The effect of the bath on the system is described by random force $F(t)$ and friction with a memory function $f(t-t')$. Equation (1) is one of the possible forms of the quantum Langevin equation and is derived, for instance, in Chapter 3 of Ref. 48.

In the Markov approximation with delta memory function,

$$f(t-t') = 2\gamma\delta(t-t'), \quad (2)$$

Eq. (1) simplifies to

$$\frac{dY}{dt} = \frac{i}{\hbar}[H_{\text{sys}}, Y] - \frac{i}{2\hbar}\left[F(t) - \gamma\frac{dQ}{dt}, [Q, Y] \right]_+. \quad (3)$$

The friction constant γ is related to the random force $F(t)$ by the fluctuation-dissipation theorem, which for thermal bath in one dimension takes the form

$$\overline{F(t)F(t')} = 2mk_B T\gamma\delta(t-t'). \quad (4)$$

Here, the overbar denotes averaging over realizations of the random process.

The system is described by a Hamiltonian H with kinetic energy $P^2/2m$ and a potential V_{sys}, which only depends on the coordinate Q. In present, the focus is on the evolution of the expectation values of the classical-like position and momentum operators and their higher-order products. To second order,

$$\frac{dQ}{dt} = \frac{P}{m},$$

$$\frac{dP}{dt} = \frac{i}{\hbar}[V_{\text{sys}}, P] + F - \gamma P,$$

$$\frac{dQ^2}{dt} = \frac{2(PQ)_s}{m},$$

$$\frac{dP^2}{dt} = \frac{i}{\hbar}[V_{\text{sys}} P^2] + 2(PF)_s - 2\gamma P^2,$$

$$\frac{d(PQ)_s}{dt} = \frac{i}{\hbar}[V_{\text{sys}} (PQ)_s] + \frac{P^2}{m} + (QF)_s - \gamma(PQ)_s. \quad (5)$$

Here, $(PQ)_s = (PQ + QP)/2$ and, correspondingly, $(PF)_s$ and $(QF)_s$ are the symmetrized products of noncommuting operators. Using the properties of the commutator relations and the fact that $[V, Q] = 0$ the last two equations can be written as

$$\frac{dP^2}{dt} = \frac{i}{\hbar}[P, [V_{\text{sys}}, P]]_+ + 2(PF)_s - 2\gamma P^2,$$

$$\frac{d(PQ)_s}{dt} = \frac{i}{2\hbar}[Q, [V_{\text{sys}}, P]]_+ + \frac{P^2}{m} + (QF)_s - \gamma(PQ)_s. \quad (6)$$

Taylor expansion of the potential around $q = \langle Q \rangle$ gives

$$\frac{dQ}{dt} = \frac{P}{m},$$

$$\frac{dP}{dt} = -\sum_{k=1}^{n} \frac{1}{(k-1)!} V^{(k)}(q)(Q-q)^{k-1} + F - \gamma P,$$

$$\frac{dQ^2}{dt} = \frac{2(PQ)_s}{m},$$

$$\frac{dP^2}{dt} = -\left[P, \sum_{k=1}^{n} \frac{1}{(k-1)!} V^{(k)}(q)(Q-q)^{k-1}\right]_+ \qquad (7)$$
$$+ 2(PF)_s - 2\gamma P^2,$$

$$\frac{d(PQ)_s}{dt} = -\frac{1}{2}\left[Q, \sum_{k=1}^{n} \frac{1}{(k-1)!} V^{(k)}(q)(Q-q)^{k-1}\right]_+$$
$$+ \frac{P^2}{m} + (QF)_s - \gamma(PQ)_s.$$

The evolution for the observable expectation values of the quantum operators taken with respect to an initial condition follows from Eqs. (7):

$$\frac{d\langle Q\rangle}{dt} = \frac{\langle P\rangle}{m},$$

$$\frac{d\langle P\rangle}{dt} = -\sum_{k=1} \frac{1}{(k-1)!} V^{(k)}(q)\langle (Q-q)^{k-1}\rangle + \langle F\rangle - \gamma\langle P\rangle,$$

$$\frac{d\langle Q^2\rangle}{dt} = \frac{2\langle PQ\rangle_s}{m},$$

$$\frac{d\langle P^2\rangle}{dt} = -\sum_{k=1} \frac{1}{(k-1)!} V^{(k)}(q)\langle [P,(Q-q)^{k-1}]_+\rangle \qquad (8)$$
$$+ 2\langle PF\rangle_s - 2\gamma\langle P^2\rangle,$$

$$\frac{d\langle PQ\rangle_s}{dt} = -\frac{1}{2}\sum_{k=1} \frac{1}{(k-1)!} V^{(k)}(q)\langle Q(Q-q)^{k-1}\rangle + \frac{\langle P^2\rangle}{m}$$
$$+ \langle QF\rangle_s - \gamma\langle PQ\rangle_s.$$

The key simplifying approximation is made at this point by decomposing the bath terms represented by the expectation values of the second-order products into the products of the first-order expectation values, as in classical mechanics. In particular, the last two equations in (8) are approximated by

$$\frac{d\langle P^2\rangle}{dt} \approx -\sum_{k=1} \frac{1}{(k-1)!} V^{(k)}(q)\langle [P,(Q-q)^{k-1}]_+\rangle$$
$$+ 2\langle P\rangle\langle F\rangle - 2\gamma\langle P\rangle^2,$$

$$\tag{9}$$

$$\frac{d\langle PQ\rangle_s}{dt} \approx -\frac{1}{2}\sum_{k=1} \frac{1}{(k-1)!} V^{(k)}(q)\langle Q(Q-q)^{k-1}\rangle + \frac{\langle P^2\rangle}{m}$$
$$+ \langle Q\rangle\langle F\rangle - \gamma\langle P\rangle\langle Q\rangle,$$

The noise F and friction γ terms now contain only expectation values of the first-order operators and, as before, are related by the fluctuation-dissipation theorem (4).

Introduction of the reduced variables

$$q \equiv \langle \hat{Q}\rangle, \quad p \equiv \langle \hat{P}\rangle,$$

$$s_q \equiv \langle \hat{Q}^2\rangle - \langle \hat{Q}\rangle^2,$$

$$\tag{10}$$

$$s_p \equiv \langle \hat{P}^2\rangle - \langle \hat{P}\rangle^2,$$

$$r \equiv \langle \hat{P}\hat{Q}\rangle_s - \langle \hat{P}\rangle\langle \hat{Q}\rangle,$$

simplifies Eqs. (8) and (9). At the second-order level all terms involving expectation values of the third- and higher-order products of P and Q are decomposed by closure into products of the first- and second-order expectation values. The closure is described explicitly in Ref. 23 for third- and fourth-order terms and in Ref. 26 for the fifth-order terms. It is consistent within QHD-2 to Taylor expand the potential V_{sys} to an odd order, since only in this case the total energy is conserved and the semiclassical dynamics can be conveniently mapped onto classical dynamics in an extended phase space.[27] Explicit Taylor expansion of the potential to the fifth order and decomposition of all products of P and Q into the first- and second-order products give

$$\frac{dq}{dt} = \frac{p}{m},$$

$$\frac{dp}{dt} = -\left[V'(q) + \frac{1}{2}V^{(3)}(q)s_q + \frac{1}{8}V^{(5)}(q)s_q^2\right] + F - \gamma p,$$

$$\frac{ds_p}{dt} = \frac{2r}{m},$$

$$\tag{11}$$

$$\frac{ds_p}{dt} = -[2V^{(2)}(q)r + V^{(4)}(q)s_q r],$$

$$\frac{dr}{dt} = -\frac{1}{2}[2V^{(2)}(q)s_q + V^{(4)}(q)s_q^2] + \frac{s_p}{m}. \qquad (11)$$

The friction and noise are now present only in the equation for $p \equiv \langle \hat{P}\rangle$, in contrast with Eqs. (8) and (9) for the original variables, where the effect of the bath is seen in both first- and second-order equations. The noise and friction terms have disappeared from the second-order equations for the reduced variables because of the classical approximation for the bath terms in (9).

As noted in Ref. 27, in addition to the total energy,

$$E = \frac{p^2 + s_p}{2m} + V(q) + \frac{1}{2}V^{(2)}(q)s_q + \frac{1}{8}V^{(4)}(q)s_q^2. \quad (12)$$

QHD-2 conserves the Heisenberg uncertainty $s_p s_q - r^2$, for instance, the minimal uncertainty

$$s_p s_q - r^2 = \hbar^2/4. \quad (13)$$

a constant of motion in the absence of bath, the uncertainty is constant motion in the absence of bath and is still conserved in the presence of the classical bath, since the second-order terms in (11) are decoupled from the bath. The conservation of (13) can be used to eliminate one of the second-order variables (10) such that the remaining four variables,

$$q \equiv \langle Q \rangle, \quad p \equiv \langle P \rangle,$$

$$s \equiv \sqrt{s_q} \equiv \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}, \quad (14)$$

$$p_s \equiv \frac{r}{\sqrt{s_q}} \equiv \frac{\langle PQ \rangle_s - \langle P \rangle \langle Q \rangle}{\sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}},$$

form two pairs of conjugate positions and momenta evolving according to

$$\frac{dq}{dt} = \frac{p}{m},$$

$$\frac{dp}{dt} = -\left[V'(q) + \frac{1}{2}V^{(3)}(q)s^2 + \frac{1}{8}V^{(5)}(q)s^4 \right] + F - \gamma p,$$

$$\frac{ds}{dt} = \frac{p_s}{m}, \quad (15)$$

$$\frac{dp_s}{dt} = -\left[V^{(2)}(q)s + \frac{1}{2}V^{(4)}(q)s^3 \right] + \frac{\hbar^2}{4ms^3}.$$

Provided that the Taylor expansion is performed to an odd order, such that every $V^{(2n)}$ term in the equation for p_s is accompanied by a $V^{(2n+1)}$ term in the equation for p, the dynamics in (15) can be interpreted[27] as those for a classical two-dimensional system with Hamiltonian,

$$H(p,q,p_s,s) = \frac{p^2 + p_s^2}{2m} + V(q) + \frac{1}{2}V^{(2)}(q)s^2 + \frac{1}{8}V^{(4)}(q)s^4$$

$$+ \frac{\hbar^2}{8ms^2}, \quad (16)$$

where the (q,p) degree of freedom couples to the classical heat bath. The $\hbar^2/8ms^2$ term arises from the Heisenberg uncertainty [Eq. (13)] contributes to ZPE, and creates a repulsive wall that keeps the width variable s positive.[27,49,50] The decoupling of the heat bath from the quantum width s arises at present due to the decomposition of the friction and noise terms to the classical level, Eqs. (8) and (9). A similar result is seen in Refs. 51 and 52 for a system linearly coupled to a bath of harmonic oscillators, with both system and bath described explicitly at the second-order level. In the QHD clo-

sure language, the system-bath coupling in Refs. 51 and 52 is decomposed to the classical level.

Equations (15) are the final results of the present derivation for QHD-2 coupled to classical bath. The form (15) is preferred to the equivalent forms (8), (9), and (11), since the classical mapping (16) simplifies interpretation, understanding, and implementation of the developed approach. The mapped equations can be easily incorporated into existing molecular dynamics codes by introduction of the mapped potential (16) without modifications to the propagation algorithms. Stability and efficiency of classical molecular dynamics are essential, especially in applications to large systems. The quantum effects, including tunneling and ZPE can be understood and interpreted as classical dynamics on modified potential-energy surfaces.[27,49–52]

III. EXAMPLES

The formalism discussed above is illustrated with three examples, including free particle, harmonic oscillator, and the Morse oscillator designed to represent the O–H stretching motion in the flexible model of water.[53]

A. Free particle

The semiclassical Langevin (15) derived in Sec. II can be immediately applied to the free particle,

$$\frac{dq}{dt} = \frac{p}{m}, \quad \frac{dp}{dt} = F - \gamma p,$$

$$\frac{ds}{dt} = \frac{p_s}{m}, \quad \frac{dp_s}{dt} = \frac{\hbar^2}{4ms^3}. \quad (17)$$

The evolution of the classical-like q and p is decoupled from the dynamics of the second-order s and p_s variables. The noise and friction are present only in the first-order equations. The Langevin equation for p and q can be solved in the usual manner to obtain the classically expected average energy of $k_B T/2$, regardless of the initial conditions for p and q. The quantum contribution to the energy stored in s and p_s remains conserved and equal to a specified initial value, while the particle spreads to infinity $s \rightarrow \infty$.

B. Harmonic oscillator

The following semiclassical Langevin equation is obtained for the harmonic oscillator:

$$\frac{dq}{dt} = \frac{p}{m}, \quad \frac{dp}{dt} = -kq + F - \gamma p,$$

$$\frac{ds}{dt} = \frac{p_s}{m}, \quad \frac{dp_s}{dt} = -ks + \frac{\hbar^2}{4ms^3}. \quad (18)$$

As in the free-particle case, the first- and second-order variables of the harmonic oscillator are decoupled, and only the first-order variables experience the effect of the heat bath. The p and q interacting with the classical bath gain $k_B T$ of thermal energy. The energy stored in s and p_s is preserved over time and is determined by the initial conditions. The
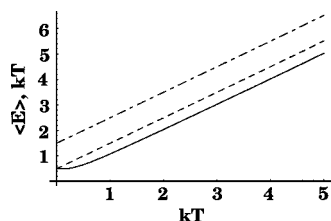
FIG. 1. Average energy generated from the semiclassical Langevin equation for the harmonic oscillator. The solid line shows the exact quantum result, the dashed line shows the results for the semiclassical Langevin equation (18) starting on the bottom of the energy surface, and the dash-dot line shows the result with one quantum of energy in the initial conditions for the semiclassical Langevin equation. See text for discussion.

minimal energy in s and p_s equals to the ZPE of the harmonic oscillator. The total thermal energy of $k_B T$ plus ZPE gives the correct quantum low-temperature limit, but deviates from the classical high-temperature limit exactly by ZPE, Fig. 1. At high temperatures ZPE is much smaller than $k_B T$ and can be neglected. Generally, the thermal equilibrium value for the average energy that follows from Eqs. (18) is equal to the classical equilibrium value plus an energy initially deposited into the s and p_s coordinates.

The free particle and harmonic oscillator constitute special examples, since their p_s and s variables are decoupled from the p and q variables and, therefore, are not affected by the bath. All four variables are coupled for more complex potentials, and the total energy reaches a thermal equilibrium independent of the initial conditions.

C. The O–H stretch of water: Morse oscillator

As an example of a nontrivial potential consider the Morse oscillator,

$$V(q) = D(1 - e^{-\alpha q})^2, \tag{19}$$

with the parameters $D = 0.708$ mdyn Å and $\alpha = 2.567$ Å^{-1} designed to represent the O–H stretching motion of liquid water.[53] The Morse potential is shown in Fig. 2(a) together with its approximation by the fourth-order Taylor expansion. Also shown are the two lowest eigenenergies of the O–H stretching mode.

The classical bath drives the first-order variables that are coupled to the second-order variables, Eq. (15). As a result, the asymptotic solution of the semiclassical Langevin equation (15) gives the average energy on the order of $k_B T$ to each degree of freedom of the Morse oscillator in the mapped QHD-2 representation. Although the thermal equilibrium is now reached in all variables independent of the initial conditions, the thermal energy is overestimated. The problem arises due to the double dimensionality of the phase space in QHD-2 relative to classical mechanics. Sampling of the states in the mapped QHD-2 phase space requires a redefinition of the Boltzmann weight, involving the change of the standard relationship $\beta = 1/k_B T$ to $\beta' = 2/k_B T$ in the high temperature and
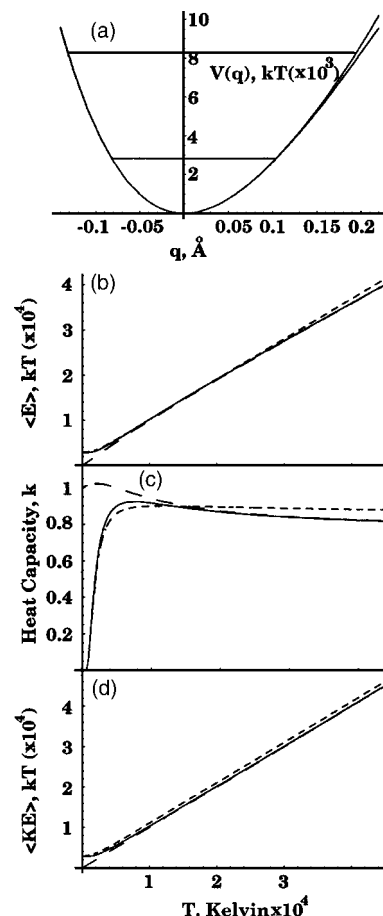

FIG. 2. Statistical quantities generated for the Morse oscillator describing the SPC-flexible stretch of water. Part (a) shows the exact potential and its approximation by quartic Taylor expansion. The horizontal lines indicate the two lowest quantum state energies. Parts (b)–(d) show the average energy, heat capacity, and average kinetic energy as functions of temperature. The solid lines give the exact quantum results, the long-dashed lines give the classical results, and the short-dashed lines are the QHD-2 results.

$$\beta' = \frac{2}{\hbar \omega}(e^{\hbar \omega / k_B T} - 1) \tag{20}$$

for arbitrary temperature.[31] The relationship (20) was obtained in reference to the harmonic oscillator with a fixed ω and can be applied to a general potential $V(q)$ by thermal averaging of the position-dependent frequency $\omega^2(q) \equiv (1/m)(d^2 V(q)/d^2 q)$,

$$\omega^2 = \frac{\int_{-\infty}^{\infty} (1/m)(d^2 V(q)/dq^2)\exp[-\beta V(q)]dq}{\int_{-\infty}^{\infty} \exp[-\beta V(q)]dq}, \tag{21}$$

in the classical Boltzmann sense.

The total energy, kinetic energy, and heat capacity of the OH stretch that follow from the semiclassical Langevin equation (15), with the noise-friction relationship (4) containing the inverse of (20) in place of $k_B T$, are shown in Fig. 2. The quantum results were obtained by diagonalization of the quartic approximation to the Morse–Hamiltonian in the harmonic-oscillator basis. The classical data were generated by integration over the phase space. The semiclassical results

show good agreement with the quantum results, particularly notable in the low-temperature region where quantum and classical mechanics disagree.

IV. CONCLUDING REMARKS

The semiclassical Langevin equation derived in this paper by application of closure to the quantum Langevin equation results in a simple technique for incorporating quantum effects into molecular-dynamics simulations. While equally simple approaches have long existed for computation of statistical averages and correlation functions,[46,47] the current approach is suitable for not only statistical averaging, but also direct real-time dynamics. The semiclassical Langevin equation (15) together with the semiclassical Boltzmann β in (20) can be used for both simulation of microcanonical and canonical dynamics and generation of canonical distributions.

The level of the current approximation is motivated by the simplicity and ease of implementation within classical molecular-dynamics codes. The system dynamics is described at the level of second-order QHD, which maps onto a classical system with doubled dimensionality and describes ZPE and moderate tunneling. Noise and friction are treated at the classical level. While higher- and lower-order approximations can be easily derived within the formalism described in present, the approximation (15) is kept at the level that can be directly applied to large systems within existing molecular-dynamics codes solely by choice of classical potential. Since higher-order QHDs do not map into classical mechanics it is not possible to utilize existing classical molecular-dynamics codes for the higher level of approximation. Work is also currently underway to extend the classical noise approximation to quantum noise; however, quantum noise is significantly more complex than classical noise.[48]

Just as the QHD approach can be used to derive the well-known equations of motion for the "frozen" and "thawed" Gaussians,[35–39] the current semiclassical Langevin equation allows one to simulate real-time Gaussian dynamics at a finite temperature. Equations (15) with the second-order Taylor expansion describe thawed Gaussians. The frozen Gaussian dynamics is given by the first two equations in (15) and a fixed s.[27]

One may consider an approximation to the quantum Langevin equation (8), where the friction terms are kept at the second order, while the noise is decomposed to the first order. This approximation can be motivated by the fact that the friction involving γ times an appropriate QHD variable is easily understood and implemented at any order, while the noise operator F can be interpreted as classical noise at the first-order expectation value, but not so at the higher orders involving system-noise products such as $\langle QF \rangle_s$ and $\langle PF \rangle_s$. Keeping the extra friction terms may also alleviate the issue associated with the extended phase-space averaging and redefinition of β, Eq. (20). Decomposing noise to the first order and friction to the second order adds $(-2\gamma s_p)$ and $(-\gamma r)$ to the equations for s_p and r in (11), respectively. The average thermal energy of free particle in such an approximation will equal $k_B T$ regardless of initial conditions, which is the correct result. The average thermal energy of the harmonic oscillator will also equal $k_B T$, since the energy stored in the second-order variables will decay to the ZPE due to the friction terms without the counterbalancing noise. The Heisenberg uncertainty product in (13) will not be conserved and will decay according to $d(s_p s_q - r^2)/dt = -2\gamma(s_p s_q - r^2)$. Thermal averages for the higher-order potentials, where the first- and second-order variables are coupled, require further study of the second order friction scheme. The limiting solutions of the generalized semiclassical Langevin equation[51,52] including memory provide another avenue for investigation. It may be expected that thermal averages obtained with various semiclassical Langevin equations that employ classical noise will agree with the quantum averages only with a redefinition of β similar to that of Eq. (20). A more rigorous resolution of this issue may require the use of quantum noise. For instance, the average thermal energy of the quantum harmonic oscillator can be recovered exactly in the QHD representation using white noise in (2) that satisfies quantum statistics with $k_B T$ in the fluctuation-dissipation relationship in (4) replaced by the thermal average of the number of harmonic quanta.[48] Application of quantum noise to QHD for a general potential is currently under investigation.

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