CONVERGENCE OF STOCHASTIC-EXTENDED LAGRANGIAN MOLECULAR DYNAMICS METHOD FOR POLARIZABLE FORCE FIELD SIMULATION

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Abstract. Extended Lagrangian molecular dynamics (XLMD) is a general method for performing molecular dynamics simulations using quantum and classical many-body potentials. Recently several new XLMD schemes have been proposed and tested on several classes of many-body polarization models such as induced dipoles or Drude charges, by creating an auxiliary set of these same degrees of freedom that are reversibly integrated through time. This gives rise to a singularly perturbed Hamiltonian system that provides a good approximation to the time evolution of the real mutual polarization field. To further improve upon the accuracy of the XLMD dynamics, and to potentially extend it to other many-body potentials, we introduce a stochastic modification which leads to a set of singularly perturbed Langevin equations with degenerate noise. We prove that the resulting Stochastic-XLMD converges to the accurate dynamics, and the convergence rate is both optimal and is independent of the accuracy of the initial polarization field. We carefully study the scaling of the damping factor and numerical noise for efficient numerical simulation for Stochastic-XLMD, and we demonstrate the effectiveness of the method for model polarizable force field systems.

Key words. Extended Lagrangian; Molecular dynamics; Polarizable force field; Singularly perturbed system; Hamiltonian system; Langevin dynamics

1. Introduction. Molecular dynamics (MD) simulations often require solving a linear or nonlinear system repeatedly for certain latent variables. For ab initio molecular dynamics simulations [18], the latent variable is the electron density. At each MD step, the electron density needs to be obtained by the self-consistent solution of the Kohn-Sham equations [12, 14], which are a set of nonlinear eigenvalue equations. In classical molecular dynamics simulation with a polarizable force field [8, 1], it is the induced dipole or Drude charge that needs to be evaluated through the solution of a linear system, typically solved to self-consistency for large systems.

In a simplified mathematical setting, the problem can be stated as follows. Let \( r \in \mathbb{R}^d \) be the collection of atomic positions, and \( x \in \mathbb{R}^{d'} \) be the collection of latent variables such as the induced dipoles. Let \( U(r) \) be a smooth external potential field involving only the atomic positions, which gives the external force

\[
F(r) = -\frac{\partial U}{\partial r}(r).
\]

Let \( Q(r, x) \) be the interaction energy involving both the atomic position and the latent variable, and we assume \( Q \) is smooth. For a given \( r \), the latent variable \( x \) is determined by the following equation

\[
\frac{\partial Q}{\partial x}(r, x) = 0.
\]
We assume the solution to (1.1) is unique for all \( r \in \mathbb{R}^d \). The molecular dynamics simulation requires the solution of the following differential-algebraic equations (DAE) system

\[
\ddot{r}_\star(t) = F(r_\star(t)) - \frac{\partial Q}{\partial r}(r_\star(t), x_\star(t)),
\]

\[
0 = -\frac{\partial Q}{\partial x}(r_\star(t), x_\star(t)),
\]

subject to certain initial conditions \( r_\star(0), \dot{r}_\star(0) \). Here the subscript \( \star \) is used to indicate the exact solution of Eq. (1.2). Note that the initial condition for \( x \) is not needed since it can be determined from \( r_\star(0) \) through Eq. (1.2b) (recall that a unique solution is assumed). To simplify the notation, we assume the mass is unity for all atomic degrees of freedom. Unless otherwise specified, we shall drop the explicit dependence on the time variable \( t \) below, and without loss of generality we assume \( d' = d \).

The polarizable force field simulation in classical molecular dynamics is an interesting and a particularly suitable case for analysis, since \( Q(r, x) \) becomes just a quadratic function with respect to the polarization field \( x \):

\[
Q(r, x) = \frac{1}{2} x^\top A(r)x - b(r)^\top x.
\]

Here for each \( r \), \( A(r) \) is a positive definite matrix, with its smallest eigenvalue uniformly bounded above 0. Hence the solution \( x(r) \) is unique for all \( r \). We also assume the mappings \( b : \mathbb{R}^d \to \mathbb{R}^d \) and \( A : \mathbb{R}^d \to \mathbb{S}^d_+ \) are smooth. Eq. (1.1) is then reduced to a simple linear equation

\[
A(r)x = b(r).
\]

This will greatly simplify our analysis in the results below.

Eq. (1.2b) or (1.4) is an algebraic system that needs to be solved at each MD time step. In molecular dynamics simulation, we are generally more interested in the accuracy of the trajectory of atoms \( r(t) \) than that of the latent variables \( x(t) \).

In the past decade, new types of integrators called the extended Lagrangian Born-Oppenheimer molecular dynamics (XL-BOMD) method [19] (initially called the time reversible molecular dynamics (TRMD) method [22]) have been developed. The main idea of XL-BOMD is to write down an extended Lagrangian for the latent variable. Instead of being solved through an algebraic system at each time step, the latent variables are evolved together with the atomic positions. XL-BOMD differs from previous extended Lagrangian molecular dynamics (XLMD) integration schemes such as Car-Parrinello molecular dynamics [7] by eliminating the coupling or mass parameter of the latent variables. Numerical results demonstrate that this strategy can significantly reduce the number of self-consistent iterations [22, 19, 2], and in some cases fully eliminate the need for performing self-consistent iteration altogether [20, 4, 3].

Following Eq. (1.2), the extended Lagrangian for the XL-BOMD approach takes the general form

\[
L_\varepsilon = \frac{1}{2} |\dot{r}_\varepsilon|^2 + \frac{\varepsilon}{2} |\dot{x}_\varepsilon|^2 - U(r_\varepsilon) - Q(r_\varepsilon, x_\varepsilon).
\]

The corresponding Euler-Lagrange equation yields

\[
\ddot{r}_\varepsilon = F(r_\varepsilon) - \frac{\partial Q}{\partial r}(r_\varepsilon, x_\varepsilon),
\]

\[
\varepsilon \ddot{x}_\varepsilon = -\frac{\partial Q}{\partial x}(r_\varepsilon, x_\varepsilon).
\]
Note that initial conditions for $x_\varepsilon$ and $\dot{x}_\varepsilon$ are needed for (1.6): $x_\varepsilon(0)$ is often prescribed by solving the algebraic equation $0 = -\partial Q / \partial x(r_\varepsilon(0), x_\varepsilon(0))$ and $\dot{x}_\varepsilon(0)$ can be obtained by differentiating Eq. (1.2b) and then let $t = 0$. Eq. (1.6) is a Hamiltonian system, and it can be discretized with symplectic or time-reversible integrators to obtain long time stability [9]. When $\varepsilon$ is sufficiently small, we may expect that the solution of Eq. (1.6) to closely follow the exact dynamics. On the other hand, the value of $\sqrt{\varepsilon}$ (which may include an additional multiplicative factor that can be viewed as a mixing parameter) provides an upper bound of the time step of the numerical integrator [19, 4, 3]. Therefore it is desirable to choose $\varepsilon$ not too small in practice. Although Eq. (1.6) introduces a systematic error in terms of $\varepsilon$ per step, hence sacrificing the accuracy of $x(t)$ to some degree, with a properly chosen $\varepsilon$, XL-BOMD often outperforms the discretized original dynamics in terms of efficiency and long time stability while still maintaining the accuracy for $r(t)$.

From a mathematical point of view, the equations of motion (1.6) can be viewed as a set of singularly perturbed equations. To the best of our knowledge, the convergence of the general XL-BOMD schemes (1.6) as $\varepsilon \to 0$ has not been established other than in the linear response regime [17], where the coupled system can be exactly diagonalized. It is difficult to generalize the analysis to nonlinear systems. Another issue associated with Eq. (1.6) is that the equation is free of dissipation. Hence numerical error introduced by the initial condition for $x_\varepsilon$ as well as external perturbation during the simulation will be memorized throughout the simulation. To overcome this problem, a number of approaches have been developed. Niklasson and co-workers have added well-designed dissipation terms to the dynamics, and though often effective, they necessarily break time reversibility [21]. Albaugh et al. have instead introduced Nose-Hoover thermostats for the latent variables, which greatly improves the robustness of XL-BOMD since the extended system thermostat variables can also evolve with time-reversible integration [2]. With careful consideration of extended system thermostat formulations or dissipation that is time-reversible to high order, the resulting numerical schemes for XL-BOMD can be highly competitive for MD simulations, e.g. with polarizable force fields.

In this paper we consider an alternative way to account for the needed fluctuation and dissipation by introducing a stochastic thermostat through the following modified XL-BOMD scheme:

\begin{align}
\dot{r}_\xi &= F(r_\xi) - \frac{\partial Q}{\partial r}(r_\xi, x_\xi), \\
\varepsilon \dot{x}_\xi &= -\frac{\partial Q}{\partial x}(r_\xi, x_\xi) - \sqrt{\varepsilon} \gamma \dot{x}_\xi + \sqrt{2\gamma T \varepsilon^{1/4}} \dot{W}.
\end{align}

Here the subscript $\xi = (\varepsilon, T, \gamma)$ denotes the set of parameters. $T > 0$ is an artificial temperature for the latent variable, $\gamma$ is an artificial friction parameter, and $\dot{W}(t)$ is the white noise. Note that the noise is degenerate and is applied only to the $x$ component. The scaling factors of the friction term and the noise with respect to $\varepsilon$ are the proper scaling relations due to the fluctuation-dissipation relation [15, 26]. Eq. (1.7b) is a Langevin equation, and thus the system will be referred to as the Stochastic-XLMD scheme in the following discussion.

Compared to the Nose-Hoover thermostat, the use of a Langevin thermostat has better ergodicity properties and hence facilitates our analysis. The Langevin thermostat does not require propagation of auxiliary variables used in the Nose-Hoover thermostat, and hence is also computationally less expensive.
Substituting $Q(r,x)$ from Eq. (1.3) into Eq. (1.1), (1.6), and (1.7), we arrive at the exact dynamics, XL-BOMD, and Stochastic-XLMD for the polarizable force field, respectively. In particular, (1.6) together with the form (1.3) provides an alternative derivation of the recently developed inertial extended Lagrangian without self-consistent field iteration (iEL/0-SCF) method [4, 3]. The form of the Stochastic-XLMD for polarizable force fields will be given explicitly in Eq. (2.3) in section 2.

**Contribution:** The main contribution of this paper is to prove that for the polarizable force field model, the atomic dynamics of Stochastic-XLMD method converges to the exact dynamics as $\varepsilon, T \to 0$. More specifically, under proper assumptions, we prove the following bounds for 2-norm errors:

$$
E\left( \sup_{0 \leq t \leq T} |r_\varepsilon(t) - r_\varepsilon(t)| \vee |p_\varepsilon(t) - p_\varepsilon(t)| \right) \leq C \left( \varepsilon^{1/2} + \varepsilon^{1/4}T^{1/2} + T \right).
$$

Here $p_\varepsilon(t) = \dot{r}_\varepsilon(t)$ is the momentum for the exact dynamics, and similarly $p_\varepsilon(t) = \dot{r}_\varepsilon(t)$, $a \vee b$ stands for the maximum of $a$ and $b$. Our proof is based on the method of averaging (see e.g. [27]). In particular, when the temperature $T \sim \varepsilon^{1/2}$, the convergence rates for both $r_\varepsilon$ and $p_\varepsilon$ are $O(\varepsilon^{1/2})$. Since $\varepsilon^{-1/2}$ is proportional to the highest frequency of the latent dynamics $x_\varepsilon$, the convergence rate is optimal.

One feature of the Stochastic-XLMD method is that in contrast to the behavior of the XL-BOMD method, the convergence rate does not depend on the accuracy of the initial condition of the latent variable $x(0), \dot{x}(0)$ (from solving the algebraic equation at $t = 0$). This is because Stochastic-XLMD has a damping factor, and the numerical error on the latent variable can only affect the dynamics within a finite time interval. We study the efficiency of Stochastic-XLMD with respect to the choice of the damping factor $\gamma$, which indicates that $\gamma$ should be generally $O(1)$ in order to minimize the numerical error. This confirms the proper scaling relation with respect to $\varepsilon$ in Eq. (1.7), and that the dissipation term $\gamma \dot{x}_\varepsilon$ should not be too large in order to avoid a strong perturbation of the time-reversible microcanonical dynamics [21]. Numerical results for model polarizable force field systems verify our theoretical estimates. We also performed numerical results for systems with non-quadratic interaction energy with respect to latent variable $x$, and the numerical behavior is similar to that of the polarizable force field models.

**Organization:** The rest of the paper is organized as follows. We study the limit when $\varepsilon, T \to 0$ in terms of time averaging and state the main result, Theorem 1 in section 2. The proof of the main theorem is given in section 3. The results are justified by numerical results in section 4, followed by conclusion and discussion in section 5.

**2. Method of time averaging.** In the discussion below, we denote the momentum variables by $p$ and $y$, such that $p_\varepsilon, p_\varepsilon$ are the first order time derivatives of $r_\varepsilon, r_\varepsilon$, respectively, and $y_\varepsilon = \sqrt{\varepsilon} \dot{x}_\varepsilon$ is the rescaled time derivative of $x_\varepsilon$. For the polarizable force field model with a quadratic interaction energy (1.3), the exact dynamics (1.2) can be rewritten as

\begin{align}
\dot{r}_\varepsilon &= p_\varepsilon, \\
\dot{p}_\varepsilon &= F(r_\varepsilon) - \left[ \frac{1}{2} x_\varepsilon^\top \frac{\partial A}{\partial r}(r_\varepsilon) x_\varepsilon - \frac{\partial b}{\partial r}(r_\varepsilon)^\top x_\varepsilon \right], \quad (2.1) \\
0 &= b(r_\varepsilon) - A(r_\varepsilon) x_\varepsilon,
\end{align}

with initial values $r_\varepsilon(0)$ and $p_\varepsilon(0)$. Since the evolution of the latent variable $x_\varepsilon$ is determined by the evolution of $r_\varepsilon$ via $x_\varepsilon = A(r_\varepsilon)^{-1} b(r_\varepsilon)$, we can then eliminate the
\( x \) variable and equivalently write the dynamical system as

\[
\begin{align*}
\dot{r}_* &= p_*, \\
\dot{p}_* &= F(r_*) - \left[ \frac{1}{2} b(r_*)^\top A(r_*)^{-1} \frac{\partial A}{\partial r}(r_*) A(r_*)^{-1} b(r_*) - \frac{\partial b}{\partial r}(r_*)^\top A(r_*)^{-1} b(r_*) \right].
\end{align*}
\]

(2.2)

Following Eq. (1.7), the corresponding Stochastic-XLMD method reads

\[
\begin{align*}
\dot{r}_\xi &= p_\xi, \\
\dot{p}_\xi &= F(r_\xi) - \left[ \frac{1}{2} x_\xi^\top \frac{\partial A}{\partial r}(r_\xi) x_\xi - \frac{\partial b}{\partial r}(r_\xi)^\top x_\xi \right], \\
\dot{x}_\xi &= \varepsilon^{-1/2} y_\xi, \\
\dot{y}_\xi &= \varepsilon^{-1/2} [b(r_\xi) - A(r_\xi) x_\xi] - \varepsilon^{-1/2} \gamma y_\xi + \varepsilon^{-1/4} \sqrt{2\gamma T} \dot{W},
\end{align*}
\]

(2.3)

where \( \varepsilon, \gamma \) and \( T \) are positive parameters, and \( W(t) \) is the standard Brownian motion.

The last equation in (2.3) is a stochastic differential equation (SDE) whose rigorous interpretation follows the Itô integral formulation, which can be simplified in this case as

\[
\begin{align*}
y_\xi(t) - y_\xi(0) &= \varepsilon^{-1/2} \int_0^t [b(r_\xi(s)) - A(r_\xi(s)) x_\xi(s)] ds \\
&\quad - \varepsilon^{-1/2} \int_0^t \gamma y_\xi(s) ds + \varepsilon^{-1/4} \sqrt{2\gamma T} W(t).
\end{align*}
\]

Since we are mainly interested in the atomic dynamics, the initial values are assumed to be accurate, i.e. \( r_\xi(0) = r_*(0), p_\xi(0) = p_*(0) \). Note that we only assume \( x_\xi(0), y_\xi(0) \) are chosen deterministically. In particular, we do not necessarily have \( x_\xi(0) = x_*(0) \).

If \( \gamma = T = 0 \), the SDE (2.3) degenerates to a singularly perturbed ODE, which is exactly the XL-BOMD approach (1.6). In this case, numerical results show that the convergence of \( r_\xi \) to \( r_* \) depends sensitively on the initial value of \( x(0) \). Figure 2.1 shows that with the inaccurate initial guess for \( x(0) \), the XL-BOMD approach gives inaccurate dynamics, while the Stochastic-XLMD approach gives a much more accurate approximation (see section 4.1 for the detailed setup). Here we plot the trajectories of the first entries of \( r \) and \( x \), and the total energy.

The difference of the convergence behaviors can be explained by the method of time averaging in multiscale analysis. Note that the fast dynamics in the XL-BOMD approach is not ergodic. In fact, the fast dynamics in that case is a Hamiltonian ODE. Thus any smooth function of the Hamiltonian will lie in the null space of the corresponding generator. Therefore, the error of the initial values will be carried through the entire simulation. We refer readers to [6] for an explicit example on how the initial values influence the entire Hamiltonian dynamics (with strong constraining potential).

However, in Stochastic-XLMD, the fast Langevin dynamics is ergodic [15, 26], which means that the stationary movement of \((x, y)\) is independent of the initial values. Consider the following Langevin dynamics with \( \varepsilon = 1 \) and fixed \( r \) viewed as a parameter (and we omit the explicit dependence on \( r \) in notations for clarity),

\[
\begin{align*}
\dot{x} &= y, \\
\dot{y} &= b - Ax - \gamma y + \sqrt{2\gamma T} \dot{W}.
\end{align*}
\]

(2.4)
The system (2.4) is ergodic with an invariant probability density

$$\rho_\infty(x, y; r) \propto \exp \left( -\frac{|y|^2}{2T} \right) \exp \left( -\frac{(x - A^{-1}b)^\top A(x - A^{-1}b)}{2T} \right).$$

That is, as $t \to \infty$, the solution $(x, y)$ of Eq. (2.4) will converge in distribution to the invariant distribution regardless of the initial values.

Now we go back to Stochastic-XLMD (2.3) and apply the method of averaging. Note that the time scale of the oscillation of $x_\xi$ and $y_\xi$ is $O(\varepsilon^{1/2})$. If we consider an
intermediate time period \([t_1, t_2]\), for example, \(t_2 - t_1 = \mathcal{O}(\varepsilon^{1/4})\), then within this time period the variable \(r_\varepsilon\) almost remains constant, and the fast variable \(x_\varepsilon\) has already converged to the invariant distribution. Therefore when \(\varepsilon\) is small, it is reasonable to reckon that the slow dynamics of \(r_\varepsilon, p_\varepsilon\) can be approximated by the averaged dynamics, in which the fast variable \(x_\varepsilon\) is averaged out with respect to the invariant measure. This can also be formally derived by the multiscale expansion method (see for example [27, Chapter 10]).

More specifically, let the averaged dynamics be defined as
\[
\dot{\tau} = \bar{p},
\]
\[
\bar{p} = F(\tau) - \int_{\mathbb{R}^{2d}} \left[ \frac{1}{2} x + \frac{\partial A}{\partial r}(\tau)x - \frac{\partial b}{\partial r}(\tau)^T x \right] p_\infty(x,y;\tau) dxdy.
\]  
(2.5)

After explicit evaluation of the integral (see the end of section 3.2 for details), we arrive at
\[
\dot{\tau} = \bar{p},
\]
\[
\bar{p} = F(\tau) - \left[ \frac{1}{2} b(\tau)^T A(\tau)^{-1} \frac{\partial A}{\partial r}(\tau) A(\tau)^{-1} b(\tau) - \frac{\partial b}{\partial r}(\tau)^T A(\tau)^{-1} b(\tau) \right] - Tg(\tau),
\]  
(2.6)

where \(g(r) = (g_1(r), \cdots, g_d(r))^T\),
\[
g_k(r) = \frac{1}{2} \sum_{k,l} \left( \frac{\partial A}{\partial r_k} \right)_{kl} \left( A^{-1} \right)_{kl} = \frac{1}{2} \text{Tr} \left( \frac{\partial A}{\partial r_k}^T A^{-1} \right). \]  
(2.7)

Compare with the exact MD (2.2), there is only one extra term \(-Tg(\tau)\). Therefore, we can expect that, as \(T \to 0\), the solution \((\bar{r}, \bar{p})\) of (2.6) converges to the exact solution \((r_*, p_*)\), and \((r_\varepsilon, p_\varepsilon)\) converges to the exact solution \((r_*, p_*)\) as \(\varepsilon, T \to 0\).

Since the time averaging relies on the ergodicity of the fast dynamics, it is clear that the convergence is independent of the initial value of the latent variables.

In order to study the efficiency of Stochastic-XLMD with respect to \(\gamma\), first let us consider two limiting scenarios. If \(\gamma\) is very close to 0, the fast dynamics will be very close to the XL-BOMD dynamics, which leads to inaccurate solutions if the initial condition of the latent variable is inaccurate. If \(\gamma\) is very large, the noise must also increase according to the fluctuation-dissipation relation. The fast dynamics then behaves as the Brownian dynamics, and thus it would take longer to reach the invariant distribution for a fixed \(r\). We find that the optimal choice of \(\gamma\) should be \(\mathcal{O}(1)\), and this will be confirmed by numerical results.

Now we state the main result precisely. We consider a fixed time interval \([0, t_f]\) with \(t_f\) fixed and independent of \(\varepsilon\). Throughout the paper we denote by \(|a|\) the absolute value of \(a\) if \(a\) is a scalar, and the vector 2-norm of \(a\) if \(a\) is a vector. \(|A|_2, |A|_F, \|A\|_\ast\) denote the matrix 2-norm, the matrix Frobenius norm and the matrix trace norm, respectively. We make the following assumptions:

1. \(A : \mathbb{R}^d \to \mathcal{S}^d_{++}\) is a smooth map with globally bounded \(|A|_2, \left\| \frac{\partial A}{\partial r_j} \right\|_\ast, \left\| \frac{\partial^2 A}{\partial r_j^2} \right\|_\ast\), \(j = 1, \cdots, d\). Furthermore, there exists a constant \(\kappa > 0\) such that \(A(r) \succeq \kappa\) for all \(r \in \mathbb{R}^d\).

2. \(b : \mathbb{R}^d \to \mathbb{R}^d\) is a smooth map with globally bounded \(|b|, \left\| \frac{\partial b}{\partial r_j} \right\|_\ast, \left\| \frac{\partial^2 b}{\partial r_j^2} \right\|_\ast, j = 1, \cdots, d\).

3. \(F : \mathbb{R}^d \to \mathbb{R}^d\) is a smooth map with globally bounded \(|\frac{\partial F}{\partial r_j}|_\ast, \left\| \frac{\partial^2 F}{\partial r_j^2} \right\|_\ast, j = 1, \cdots, d\).
4. Initial values for $(r_\ast, p_\ast)$, $(r_\xi,p_\xi,x_\xi,y_\xi)$ and $(\tau, \rho)$ are deterministic, with $r_\ast(0) = r_\xi(0) = \tau(0)$, $p_\ast(0) = p_\xi(0) = \rho(0)$.
5. For $0 < T < 1$, $0 < \varepsilon < 1$, $\gamma > 0$, the solution $(\tau, \rho)$ is bounded independently of $T$, and the solution $(r_\xi,p_\xi,x_\xi,y_\xi)$ is bounded in the sense that

$$
E \left( \sup_{0 \leq t \leq t_f} |x_\xi(t)|^2 \right), \quad E \left( \sup_{0 \leq t \leq t_f} |y_\xi(t)|^2 \right),
$$

$$
E \int_0^{t_f} |r_\xi(s)|^4 ds, \quad E \int_0^{t_f} |p_\xi(s)|^4 ds, \quad E \int_0^{t_f} |x_\xi(s)|^4 ds, \quad E \int_0^{t_f} |y_\xi(s)|^4 ds
$$

are bounded independently of $\varepsilon, T$ and $\gamma$.

Here the first three assumptions assure the existence and uniqueness of the smooth, globally bounded solutions of (2.1) and (2.6), together with the existence and uniqueness of the solution of (2.3). It is worth mentioning that weakening all the assumptions is possible by proving some *a priori* bounds, but we limit ourselves to the simple setup for expository purposes. Throughout this paper, $C$ will denote a sufficiently large constant of possibly varying size, which is independent of $\xi$ but may depend on other constant factors such as the final time $t_f$ and the dimension $d$.

**THEOREM 1.** Let $(r_\ast, p_\ast)$ solve the exact MD (2.2) and $(r_\xi,p_\xi,x_\xi,y_\xi)$ solve the Stochastic-XLMD (2.3). Then for any $0 < \varepsilon < 1$, $0 < T < 1$, $\gamma > 0$ there exists a constant $C > 0$ such that

$$
E \left( \sup_{0 \leq t \leq t_f} |r_\xi(t) - r_\ast(t)| \lor |p_\xi(t) - p_\ast(t)| \right)
$$

$$
\leq C \left[ \left( \frac{1}{\delta_\gamma} + \frac{1}{\delta_\gamma^2} \right) \varepsilon^{1/2} + \left( \frac{\gamma}{\delta_\gamma^2} + 1 \right) \varepsilon^{1/4} T^{1/2} + T + \frac{\gamma}{\delta_\gamma} \varepsilon^{1/2} T \right],
$$

where $\delta_\gamma$ is a $\gamma$-dependent positive real number defined as

$$
\delta_\gamma = \begin{cases} 
\gamma/4, & 0 < \gamma \leq 2\sqrt{\kappa}, \\
(\gamma - \sqrt{\gamma^2 - 4\kappa})/4, & \gamma > 2\sqrt{\kappa}.
\end{cases} \quad (2.8)
$$

Before proceeding with the proof in section 3, several remarks are in order.

Theorem 1 verifies the intuition that $\varepsilon$ and $T$ should be small to yield a reasonable approximation, and provides the convergence order with respect to $\varepsilon$ and $T$. More specifically, if we fix $\gamma$ and all other parameters such as $t_f$, then the dominating part of errors becomes $O(\varepsilon^{1/2} + \varepsilon^{1/4} T^{1/2} + T)$, which suggests the optimal strategy for choosing parameters should be $T = O(\varepsilon^{1/2})$. Therefore the optimal convergence order with respect to $\varepsilon$ is $1/2$. The optimality of the convergence order will be verified by numerical results in section 4. Theorem 1 also suggests that $\gamma$ should not be too large or too small. For fixed $\varepsilon$ and $T$, the error bounds will go to infinity if $\gamma \to 0$ or $\gamma \to \infty$. We also remark that the constant $C$ depends exponentially on $t_f$ due to the use of Gronwall’s inequality.

The convergence of XL-BOMD type schemes in the linear response regime has been studied in [17], where the energy depends quadratically both with respect to $r$ and $x$. In such a case, the dynamics is diagonalizable, and the convergence of XL-BOMD can be studied using perturbation theory with respect to the eigenvalues of the
diagonalized systems. Such a strategy cannot be used for the polarizable force field model, in which the energy is non-quadratic with respect to $r$, though it is quadratic with respect to $x$.

A rigorous proof of the method of averaging for model SDEs is given in [27, Chapter 17], where the generator of the auxiliary SDE is assumed to be a non-degenerate elliptic operator and the domain of interest is assumed to be compact. From the technical perspective, the key of the proof is to apply the Itô formula to the solution of the Poisson equation (3.5). The aforementioned assumptions facilitates the growth estimate of the solution of the Poisson equation corresponding to the SDE. Our proof generalizes the method to the Stochastic-XLMD case, where the generator of the Langevin equation is a degenerate elliptic operator, and the domain is the whole space $\mathbb{R}^d$, which requires a more careful study of the Poisson equation (3.5).

The existence and uniqueness of a smooth solution to the Poisson equation can be assured in a more general case than the quadratic interaction energy [16, 11]. Under proper assumptions such that the interaction energy satisfies the Poincaré inequality and grows moderately (both of which the quadratic interaction energy satisfies), the generator is invertible within the space $\{u \in H^1(d\mu) : \int u d\mu = 0\}$ where $d\mu$ is the invariant measure. This is a result from hypocoercivity [29], which focuses on the convergence to the stationary state for certain classes of degenerate diffusive equations. The smoothness of the solution is a straightforward result from the hypoellipticity [26], which can be traced back to Hörmander [13].

We would also like to mention a series of papers [23, 24, 25], which provide a more general study of the solution of the Poisson equation on $\mathbb{R}^d$ both for the non-degenerate case and the degenerate case. The solution of the Poisson equation in our proof (Eq. (3.7)) originates from [25]. Our work generalizes the results of [25, 28] (though for a much simpler scenario), in the sense that we can describe the explicit dependence of the constant on parameters such as $\gamma, \varepsilon, T$, which is needed for the convergence rate of the Stochastic-XLMD scheme.

3. Proof of the main theorem. In this section we prove Theorem 1 through combining the following two theorems.

**Theorem 2.** Let $(\bar{r}, \bar{p})$ solve the averaged dynamics (2.6) and $(r_{\xi}, p_{\xi}, x_{\xi}, y_{\xi})$ solve the Stochastic-XLMD (2.3). Then for any $0 < \varepsilon < 1$, $0 < T < 1$, $\gamma > 0$ there exists a constant $C > 0$ such that

$$E \left( \sup_{0 \leq t \leq T} |r_{\xi}(t) - \bar{r}(t)| \vee |p_{\xi}(t) - \bar{p}(t)| \right) \leq C \left( \left( \frac{1}{\delta_x} + \frac{1}{\delta^2_x} \right) \varepsilon^{1/2} + \left( \frac{\gamma}{\delta^2_x} + 1 \right) \varepsilon^{1/4} T^{1/2} + \frac{\gamma}{\delta^2_x} \varepsilon^{1/2} T \right).$$

**Theorem 3.** Let $(r_*, p_*)$ solve the exact dynamics (2.2) and $(\bar{r}, \bar{p})$ solve the averaged dynamics (2.6). Then for any $0 < T < 1$, there exists a constant $C > 0$ such that

$$\sup_{0 \leq t \leq t_f} |\bar{r}(t) - r_*(t)| \vee |\bar{p}(t) - p_*(t)| \leq CT.$$
Theorem 3 is a direct result from the theorem of Alekseev and Gröbner [10, Theorem 14.5]. In order to prove Theorem 2, we generalize the method in [27, Chapter 17], where the key is to apply the Itô formula to the solution of the Poisson equation corresponding to Langevin dynamics. The rest of the proof is organized as follows. In section 3.1 we first record some useful properties of the Langevin dynamics (2.4). We then discuss the solution of the Poisson equation in section 3.2. The proof of Theorem 2 and 3 follows in section 3.3.

3.1. Properties of Langevin Dynamics. We first study the linear SDE (2.4) with fixed $r$, of which the solution can be obtained explicitly. We remark that despite the $r$ dependence in $A$ and $b$, the bounds of $b$ and $A^{-1}$ are independent of $r$ by assumption 1 and 2.

We start with the standard ergodic property of Langevin dynamics. The proof of Proposition 4 can be found in e.g. [26, Prop. 6.1 and section 3.7].

Proposition 4. Let $(x(t), y(t))$ denote the solution of SDE (2.4) and the adjoint of $L_0$ is denoted $L_0^*$. Then the probability density function of $z(t)$ is the solution of the Fokker-Planck equation

$$
\frac{d}{dt} \rho_t = L_0^* \rho_t.
$$

Furthermore, the density function is explicitly given by

$$
\rho_t(z) = \frac{1}{Z_t} \exp \left[ -\frac{1}{2} (z - e^{-3t} z(0))^\top G_t^{-1} (z - e^{-3t} z(0)) \right],
$$

where $G_t$ is given by

$$
G_t = \int_0^t e^{-3s} \begin{pmatrix} 0 & 0 \\ 0 & 2\gamma T d \end{pmatrix} e^{-3s} ds
$$

and $Z_t$ is the normalization constant

$$
Z_t = (2\pi)^d \sqrt{\det G_t}.
$$

(b) The SDE (2.4) is ergodic.
(c) There exists a unique invariant density $\rho_\infty(x; y; r) \in C^\infty(\mathbb{R}^d \times \mathbb{R}^d; \mathbb{R}^d)$ such that

$$
L_0^* \rho_\infty = 0, \quad \rho_\infty > 0.
$$

Furthermore, the invariant measure is a Gaussian distribution in terms of $z$, which is mean-zero and its covariance matrix $G_\infty$ is defined by (3.3) after taking the limit $t \to \infty$. Equivalently, in terms of $x$ and $y$, the invariant density $\rho_\infty$ is given by

$$
\rho_\infty = \frac{1}{Z_\infty} \exp \left( \frac{|y|^2}{2T} \right) \exp \left( -\frac{(x - A^{-1} b)^\top A(x - A^{-1} b)}{2T} \right),
$$
where $Z_\infty$ is the normalization constant

$$Z_\infty = (2\pi)^d T^d \left( \sqrt{\det A} \right)^{-1}.$$  

The convergence rate of the covariance matrix $\mathcal{S}_t$ towards $\mathcal{S}_\infty$ is recorded in Proposition 5.

**Proposition 5.** Let $\delta_\gamma$ denote the positive real number defined in Eq. (2.8). Then there exists a constant $C > 0$ such that

(a) $\|e^{-Bt}\|_2 \leq Ce^{-\delta_\gamma t},$

(b) $\|\mathcal{S}_t - \mathcal{S}_\infty\|_2 \leq C \gamma \delta_\gamma T e^{-2\delta_\gamma t}.$

**Proof.** See Appendix A.

3.2. Poisson Equation. Define

$$h(r, x) := F(r) - \left( \frac{1}{2} x \gamma A x - \left( \frac{\partial b}{\partial r} \right)^\top x \right).$$  \hspace{1cm} (3.4)

We are interested in the following Poisson equation corresponding to the Langevin dynamics.

$$L_0 \phi(x, y; r) = h(r, x) - \int_{\mathbb{R}^2d} h(r, x') \rho_\infty(x', y'; r) dy' dx',$$

$$\int_{\mathbb{R}^2d} \phi(x, y; r) \rho_\infty(x, y; r) dy dx = 0.$$  \hspace{1cm} (3.5)

**Proposition 6.** For any $0 < T < 1$, $\gamma > 0$, there exists a smooth function $\phi(x, y; r)$ which solves the Poisson equation (3.5) and satisfies the estimates

$$|\phi(r, x, y)| \leq C \left[ \frac{\gamma}{\delta_\gamma^2} T + \frac{1}{\delta_\gamma} (1 + |x|^2 + |y|^2) \right],$$

$$\|\nabla_{(x,y)} \phi(r, x, y)\|_F \leq C \frac{1}{\delta_\gamma} (1 + |x| + |y|),$$

$$\|\nabla_r \phi(r, x, y)\|_2 \leq C \left[ \frac{\gamma}{\delta_\gamma^2} T + \frac{1}{\delta_\gamma} (1 + |x|^2 + |y|^2) + \frac{\gamma}{\delta_\gamma^3} T + \frac{1}{\delta_\gamma^2} (1 + |x|^2 + |y|^2) \right].$$  \hspace{1cm} (3.6)

where $C$ is a positive constant which is independent of $\gamma, T, r, x, y$.

**Proof.** The proof is constructive. Let

$$f(x, y; r) = h(r, x) - \int_{\mathbb{R}^2d} h(r, x') \rho_\infty(x', y'; r) dy' dx'.$$

Define

$$v(x, y, t; r) = E_{x,y} f(x(t), y(t); r),$$
and

\[
\phi(x, y; r) = -\int_0^\infty v(x, y, s; r) ds \\
= -\int_0^\infty \left[ E_{x,y} h(r, x(s)) - \int_{\mathbb{R}^d} h(r, x') \rho_\infty(x', y'; r) dy' dx' \right] ds.
\] (3.7)

Here \(E_{x,y}\) means the expectation with respect to \((x(t), y(t))\), which is the solution to the SDE (2.4) with initial values \(x(0) = x, y(0) = y\).

We organize the proof in a few steps below.

(1) \(\phi\) is well-defined. The key observation is that \(h\) is a quadratic function in \(x\). Hence \(E_{x,y} h(r, x(s))\) can be computed explicitly as \(x(s)\) is a Gaussian random variable by Proposition 4. Specifically, we still use the notations in Proposition 4 and let \(\mathcal{D}(s)\) denote the top \(d\) rows of the matrix \(e^{-2s} \mathcal{D}\), then

\[
E_{x,y} h_k(r, x(s)) = E_{x,y} \left[ F_k(r) - \left( \frac{1}{2} x(s) \frac{\partial A}{\partial r_k} x(s) - \frac{\partial b}{\partial r_k} x(s) \right) \right] \\
= F_k(r) - E_{x,y} \left( \frac{1}{2} x(s) - E_{x,y} x(s) \right) \frac{\partial A}{\partial r_k} (x(s) - E_{x,y} x(s)) \\
- \frac{1}{2} E_{x,y} x(s) \frac{\partial A}{\partial r_k} E_{x,y} x(s) + \frac{\partial b}{\partial r_k} E_{x,y} x(s) \\
= F_k(r) - \frac{1}{2} \text{Tr} \left( \frac{\partial A}{\partial r_k} \mathcal{G}_k^{11} \right) - \frac{1}{2} \left( A^{-1} b + \mathcal{D}(s) b \right) \frac{\partial A}{\partial r_k} A^{-1} b + \frac{\partial b}{\partial r_k} A^{-1} b.
\]

where \(\mathcal{G}_k^{11}\) is the upper-left \(d \times d\) block matrix of \(\mathcal{G}_k\).

The second part of the integrand in Eq. (3.7) is the expectation with respect to \(x', y'\) with density \(\rho_\infty\), which can be computed as

\[
\int_{\mathbb{R}^d} h_k(r, x') \rho_\infty(x', y'; r) dy' dx' \\
= F_k(r) - \frac{1}{2} \text{Tr} \left( \frac{\partial A}{\partial r_k} \mathcal{G}_k^{11} \right) - \frac{1}{2} \left( A^{-1} b \right) \frac{\partial A}{\partial r_k} A^{-1} b + \frac{\partial b}{\partial r_k} A^{-1} b.
\] (3.8)

The integrand \(v\) in (3.7) can be hereby rewritten as

\[
v_k(x, y; s) \\
= -\frac{1}{2} \text{Tr} \left[ \frac{\partial A}{\partial r_k} (\mathcal{G}_k^{11} - \mathcal{G}_k^{11}) \right] - \frac{1}{2} \text{Tr} \mathcal{D}(s) \frac{\partial A}{\partial r_k} A^{-1} b - \frac{1}{2} b^\top A^{-1} \frac{\partial A}{\partial r_k} \mathcal{D}(s) b \\
- \frac{1}{2} b^\top \mathcal{D}(s) b + \frac{\partial b}{\partial r_k} \mathcal{D}(s) b.
\] (3.9)

By assumptions, \(\|\partial A/\partial r_k\|_\ast, |b|\) and \(\|A^{-1}\|_2\) are bounded independently of \(r\), and Proposition 5 states that \(\|\mathcal{G}_k^{11} - \mathcal{G}_k^{11}\|_2\) is bounded by \(\delta_t e^{-2\delta_t t}\) and \(\|\mathcal{D}(s)\|_2\) is bounded by \(\exp(-\delta_s s)\). Hence there exists a constant \(C > 0\) which is independent of \(x, y, r, \gamma\) and \(T\) such that

\[
\left| \text{Tr} \left[ \frac{\partial A}{\partial r_k} (\mathcal{G}_k^{11} - \mathcal{G}_k^{11}) \right] \right| \leq \left\| \frac{\partial A}{\partial r_k} \right\|_\ast \|\mathcal{G}_k^{11} - \mathcal{G}_k^{11}\|_2 \leq C \frac{\gamma}{\delta_\gamma} T e^{-2\delta_\gamma t}.
\]


We may use the operator norm to bound the other terms and have,

\[
|v_k(x, y, s; r)|
\leq C \left[ \frac{\gamma}{\delta_\gamma} T e^{-2\delta_\gamma s} + e^{-\delta_\gamma s}(1 + |x| + |y|) + e^{-2\delta_\gamma s}(1 + |x|^2 + |y|^2) \right]
\leq C \left[ \frac{\gamma}{\delta_\gamma} T e^{-2\delta_\gamma s} + e^{-\delta_\gamma s}(1 + |x|^2 + |y|^2) \right].
\] (3.10)

For fixed \(x, y\), the integrand decays exponentially in time, and thus \(\phi\) is well defined.

(2) \(\phi\) is a smooth solution to the Poisson equation. The smoothness directly follows from the computation above. The mean-zero condition with respect to \(\rho_\infty\) is straightforward from the definition of \(\phi\). The result that \(\phi\) satisfies the Poisson equation is standard from the Kolmogorov backward equation.

(3) \(\phi\) allows the estimates (3.6). In fact the first estimate directly follows from integrating (3.10) and

\[ |\phi| \leq C \left[ \frac{\gamma}{\delta_\gamma} T + \frac{1}{\delta_\gamma} (1 + |x|^2 + |y|^2) \right]. \]

Furthermore, \(\phi\) is a quadratic function of \(x\) and \(y\), then

\[
\|\nabla(x, y)\phi\|_F \leq C \left[ \frac{1}{\delta_\gamma} (1 + |x| + |y|) \right].
\]

In order to estimate \(\nabla_r\phi\), we need to first estimate \(\nabla_r \mathcal{D}(s)\) and \(\nabla_r S_t^{11}\). This can be done by applying the following formula [30]

\[
\frac{d}{dt} e^{X(t)} = \int_0^1 e^{\beta X(t)} \frac{dX(t)}{dt} e^{(1-\beta)X(t)} d\beta.
\]

We have

\[
\left\| \frac{\partial}{\partial r_k} \mathcal{D}(s) \right\|_2 \leq \left\| \frac{\partial}{\partial r_k} e^{-\beta s} \right\|_2
= C \left\| \int_0^1 e^{-\beta \mathcal{D}_s} \frac{\partial}{\partial r_k} e^{-(1-\beta)\mathcal{D}_s} d\beta \right\|_2
\leq C \int_0^1 \left\| e^{-\beta \mathcal{D}_s} \right\|_2 \left\| \frac{\partial}{\partial r_k} \right\|_2 \left\| e^{-(1-\beta)\mathcal{D}_s} \right\|_2 d\beta
\leq C s \int_0^1 e^{-\beta \mathcal{D}_s} e^{-(1-\beta)\mathcal{D}_s} d\beta
= C s e^{-\delta_\gamma s}.
\]

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Then Eq. (3.9) indicates
\[
\left\| \frac{\partial}{\partial r} \phi(x, y, s; r) \right\|_2 \leq C \left[ \frac{\gamma T}{\delta^2} e^{-2\delta_\gamma s} + e^{-\delta_\gamma s} (1 + |x| + |y|) + e^{-2\delta_\gamma s} (1 + |x|^2 + |y|^2) \right] \\
+ C \left[ \frac{\gamma T}{\delta^2} e^{-2\delta_\gamma s} + e^{-\delta_\gamma s} (1 + |x| + |y|) + e^{-2\delta_\gamma s} (1 + |x|^2 + |y|^2) \right]
\]
Integrate with respect to \( s \) and we get
\[
\| \nabla_r \phi \|_2 \leq C \left[ \frac{\gamma T}{\delta^2} + \frac{\gamma}{\delta^2} (1 + |x|^2 + |y|^2) + \frac{\gamma T}{\delta^2} + \frac{\gamma}{\delta^2} (1 + |x|^2 + |y|^2) \right].
\]

Note that in the proof of Proposition 6, we have already computed \( \int h_0 \phi \) in Eq. (3.8). This is exactly the average of the right hand side of (2.3) with respect to the invariant measure of the fast variables \( x \) and \( y \), and we obtain an explicit formulation of the averaged dynamics. Therefore the averaged equation defined as Eq. (2.5) can be equivalently given as Eq. (2.6).

3.3. Proof of Theorem 2 and 3. Since we have already obtained estimates of the solution to the Poisson equation for the degenerate Langevin generator, we can generalize the method in [27] to prove Theorem 2.
Proof. [Theorem 2] Notice that the generator for (2.3) is

$$\mathcal{L} = \frac{1}{\sqrt{\varepsilon}} \mathcal{L}_0 + \mathcal{L}_1$$

where $\mathcal{L}_0$ is given in (3.1) and

$$\mathcal{L}_1 = p \cdot \nabla_r + h(r, x) \cdot \nabla_p.$$

Now we apply the Itô formula to $\phi(x_\xi, y_\xi; r_\xi)$ and obtain

$$\frac{d\phi}{dt}(x_\xi, y_\xi; r_\xi) = \frac{1}{\sqrt{\varepsilon}} \mathcal{L}_0 \phi(x_\xi, y_\xi; r_\xi) + \nabla_r \phi(x_\xi, y_\xi; r_\xi) p_\xi$$

$$+ \sqrt{\frac{2\gamma_T}{\varepsilon^{1/4}}} \nabla_y \phi(x_\xi, y_\xi; r_\xi) \frac{dW}{dt}.$$

Let us introduce the notation

$$\bar{h}(r) = F(r) - \left( \frac{1}{2} b^\top A^{-1} \frac{\partial A}{\partial r} A^{-1} b - b^\top A^{-1} \frac{\partial b}{\partial r} \right)(r).$$

Notice that $\phi$ is the solution to the Poisson equation (3.5), and we obtain

$$\frac{dp_\xi}{dt} = h(r_\xi, x_\xi)$$

$$= \bar{h}(r_\xi) + Tg(r_\xi) + \mathcal{L}_0 \phi(x_\xi, y_\xi; r_\xi)$$

$$= \bar{h}(r_\xi) + Tg(r_\xi) + \varepsilon^{1/2} \frac{d\phi}{dt}(x_\xi, y_\xi; r_\xi)$$

$$- \varepsilon^{1/2} (\nabla_r \phi(x_\xi, y_\xi; r_\xi)) p_\xi - \varepsilon^{1/4} \sqrt{2\gamma_T} \nabla_y \phi(x_\xi, y_\xi; r_\xi) \frac{dW}{dt}.$$

We define

$$\theta(t) = \phi(x_\xi(t), y_\xi(t); r_\xi(t)) - \phi(x_\xi(0), y_\xi(0); r_\xi(0))$$

$$- \int_0^t (\nabla_r \phi(x_\xi(s), y_\xi(s); r_\xi(s))) p_\xi(s) ds,$$

and the martingale term

$$M(t) = - \int_0^t \sqrt{2\gamma_T} \nabla_y \phi(x_\xi(s), y_\xi(s); r_\xi(s)) dW(s).$$

Then we have

$$p_\xi(t) = p_\xi(0) + \int_0^t \left[ \bar{h}(r_\xi(s)) + Tg(r_\xi(s)) \right] ds + \varepsilon^{1/2} \theta(t) + \varepsilon^{1/4} T^{1/2} M(t).$$

If we compare this with the averaged equation (2.6)

$$\bar{p}(t) = \bar{p}(0) + \int_0^t \left[ \bar{h}(\bar{r}(s)) + Tg(\bar{r}(s)) \right] ds,$$

and use the initial condition $p_\xi(0) = \bar{p}(0)$, then we have

$$p_\xi(t) - \bar{p}(t) = \int_0^t \left[ \bar{h}(r_\xi(s)) - \bar{h}(\bar{r}(s)) + Tg(r_\xi(s)) - Tg(\bar{r}(s)) \right] ds$$

$$+ \varepsilon^{1/2} \theta(t) + \varepsilon^{1/4} T^{1/2} M(t).$$
For $r$ we simply have
\[ r_\xi(t) - r(t) = \int_0^t [p_\xi(s) - p(s)] \, ds. \]

Define the error function
\[ \epsilon(t) = \begin{pmatrix} r_\xi(t) - r(t) \\ p_\xi(t) - p(t) \end{pmatrix} \]
and the Lipschitz constant
\[ L = \max \left\{ 1, \sup_{r \in \mathbb{R}^d} \left\| \frac{\partial h}{\partial r} \right\|_2 + \sup_{r \in \mathbb{R}^d} \left\| \frac{\partial g}{\partial r} \right\|_2 \right\}. \]

Then for any $t \in [0, t_f]$,\[
|\epsilon(t)| \leq L \int_0^t |\epsilon(s)| \, ds + \varepsilon^{1/2} |\theta(t)| + \varepsilon^{1/4} T^{1/2} |M(t)|.\]

By Proposition 6, we obtain
\[
\sup_{0 \leq t \leq t_f} |\theta(t)| \leq C \frac{\gamma}{\delta^2} T + C \frac{1}{\delta^2} + C \frac{1}{\delta^2} \sup_{0 \leq t \leq t_f} (|x_\xi(t)|^2 + |y_\xi(t)|^2) \\
+ C \left( \frac{\gamma}{\delta^2} + \frac{\gamma}{\delta^2} \right) T \int_0^{t_f} |p_\xi(s)| \, ds \\
+ C \left( \frac{1}{\delta^2} + \frac{1}{\delta^2} \right) \int_0^{t_f} |p_\xi(s)|(1 + |x_\xi(s)|^2 + |y_\xi(s)|^2) \, ds
\]
and
\[
\mathbb{E} \left( \sup_{0 \leq t \leq t_f} |\theta(t)| \right) \leq C \left( \frac{\gamma}{\delta^2} T + \frac{\gamma}{\delta^2} T + \frac{1}{\delta^2} + \frac{1}{\delta^2} \right). \]

For the martingale term, the Itô isometry gives
\[
\mathbb{E} \left| \langle M \rangle_t \right|^2 \leq C \int_0^t 2\gamma \mathbb{E} \left\| \nabla_y \phi(r_\xi(s), x_\xi(s), y_\xi(s)) \right\|_2^2 \, ds \leq C \frac{\gamma}{\delta^2},
\]
where $\langle M \rangle_t$ is the quadratic variation of the martingale $M(t)$ (Definition 3.18, [27]).

By taking expectation of the inequality $|\langle M \rangle_t|^{1/2} \leq |\langle M \rangle_t|^{1/2} + 1$, we have
\[
\mathbb{E} |\langle M \rangle_t|^{1/2} \leq C \frac{\gamma}{\delta^2} + 1.
\]
Hence, by the Burkholder-Davis-Gundy inequality (Theorem 3.22, [27]), we obtain

\[
\mathbb{E} \left( \sup_{0 \leq t' \leq t} |e(t')| \right) \leq L \int_0^t \mathbb{E} |e(s)| ds + C \left( \frac{\gamma}{\delta^2} T + \frac{\gamma}{\delta^3} T + \frac{1}{\delta^2} \right) \varepsilon^{1/2}
\]

\[+ \varepsilon^{1/4} T^{1/2} \mathbb{E} \left( \sup_{0 \leq t' \leq t} |M(t')| \right) \]

\[\leq L \int_0^t \mathbb{E} |e(s)| ds + C \left( \frac{\gamma}{\delta^2} T + \frac{\gamma}{\delta^3} T + \frac{1}{\delta^2} \right) \varepsilon^{1/2}
\]

\[+ C \varepsilon^{1/4} T^{1/2} \mathbb{E} \left| M(t) \right|^{1/2} \]

\[\leq L \int_0^t \mathbb{E} \sup_{0 \leq \tau \leq s} |e(\tau)| ds + C \left( \frac{\gamma}{\delta^2} T + \frac{\gamma}{\delta^3} T + \frac{1}{\delta^2} \right) \varepsilon^{1/2}
\]

\[+ C \left( \frac{\gamma}{\delta^2} + 1 \right) \varepsilon^{1/4} T^{1/2}.
\]

By the integral version of the Gronwall inequality, we obtain

\[
\mathbb{E} \left( \sup_{0 \leq t' \leq t} |e(t)| \right) \leq C \left[ \left( \frac{\gamma}{\delta^2} T + \frac{\gamma}{\delta^3} T + \frac{1}{\delta^2} \right) \varepsilon^{1/2} + \left( \frac{\gamma}{\delta^2} + 1 \right) \varepsilon^{1/4} T^{1/2} \right]
\]

\[\leq C \left[ \left( \frac{1}{\delta^2} + \frac{1}{\delta^2} \right) \varepsilon^{1/2} + \left( \frac{\gamma}{\delta^2} + 1 \right) \varepsilon^{1/4} T^{1/2} + \frac{\gamma}{\delta^2} \varepsilon^{1/2} T \right].
\]

\[
\square
\]

Now we move on to Theorem 3. Compared to the exact dynamics, the averaged equation formally only involves one additional term, which can be handled by the variational equation.

**Proof.** [Theorem 3] Define \( \Psi(t, s, \eta, \zeta) \) to be the resolvent of the variational equation

\[
\dot{\Psi}(t, s, \eta, \zeta) = \left( \begin{array}{cc}
0 & I_d \\
\frac{\partial h}{\partial r}(u^{s,t}(\eta, \zeta)) & 0
\end{array} \right) \Psi(t, s, \eta, \zeta),
\]

\[
\Psi(s, s, \eta, \zeta) = I_{2d}
\]

where \( u^{s,t}(\eta, \zeta) \) is the solution to the averaged equation (2.6) with starting time at \( s \) and initial value \( r(s) = \eta \) and \( p(s) = \zeta \). By assumption 1, 2 and 3, \( \frac{\partial h}{\partial r} \) is bounded independently of \( \eta, \zeta \), thus \( \Psi \) is bounded independently of \( T \).

Then by the theorem of Alekseev and Gröbner [10, Theorem 14.5],

\[
\left( \begin{array}{c}
\tilde{r}(t) \\
\dot{\tilde{r}}(t)
\end{array} \right) = \left( \begin{array}{c}
\tilde{r}_s(t) \\
\dot{\tilde{r}}_s(t)
\end{array} \right) + T \int_0^t \Psi(t, s, \tilde{r}(s), \dot{\tilde{r}}(s)) \left( \begin{array}{c}
0 \\
g(\tilde{r}(s))
\end{array} \right) ds.
\]

We hereby obtain the desired estimate. \( \square \)

**4. Numerical examples.** In this section we verify the accuracy and the order of convergence indicated in Theorem 1. We also demonstrate the efficiency of Stochastic-XLMD in terms of the reduction of the number of SCF iterations, i.e. the number of iterations in solving Eq. (1.2b) with iterative methods. All the calculations are
carried out using MATLAB on the Berkeley Research Computing program at the University of California, Berkeley. Each node consists of two Intel Xeon 10-core Ivy Bridge processors (20 cores per node) and 64 GB of memory.

4.1. Accuracy. Let us consider a simple two dimensional model

\[ U(r) = r_1^2 + r_2^2 = |r|^2, \quad F(r) = -\frac{\partial U}{\partial r}, \]

\[ A(r) = \begin{pmatrix} 2 + |r|^2 & |r|^2 \\ |r|^2 & 1 + |r|^2 \end{pmatrix}, \]

\[ b(r) = (\sin(r_1 + r_2), \cos(r_1 - 2r_2))^T. \]

Initial values for the exact MD are

\[ r_*(0) = (0.587, -0.810)^T, \quad p_*(0) = (-1.00, 0.500)^T. \]  

Initial values for the Stochastic-XLMD are

\[ r_ξ(0) = r_*(0), \quad p_ξ(0) = p_*(0), \quad x_ξ(0) = x_*(0) + (0.500, -0.500)^T, \quad y_ξ(0) = (0, 0)^T. \]

The Verlet scheme is used to propagate the exact MD, and the BAOAB scheme [15] is used to propagate the Stochastic-XLMD. The time step size is fixed to be $5.00 \times 10^{-6}$, which is small enough for all the numerical solutions generated in this subsection to be regarded as the exact analytic solution under the same parameters. The time interval is fixed to be $[0, 5]$. We may also perform the simulation along a longer time interval. However, since we report the pointwise error along the trajectory here, we expect that the error will eventually grow exponentially with respect to the final time in accordance to the error estimate. All reported errors are the averaged errors of 10 independent simulations.

First, Theorem 1 assumes that $\gamma$ should be $O(1)$. To confirm that such choice can yield the optimal error, we adjust $\gamma$ with respect to various choices of $\varepsilon$ and $T$. Figure 4.1 indicates that in order to minimize the error, the optimal value of $\gamma$ is indeed a constant and is around $0.100$ for this example.

Now we fix $\gamma = 0.100$ and $T = 10^{-5}$ and study the dependence on $\varepsilon$. Figure 4.2 shows that under such choice of $\gamma$ and $T$, the errors of $r$ and $p$ decrease as $\varepsilon$ becomes smaller. The order of convergence, estimated using data points with $\varepsilon \leq 10^{-4}$, is 0.402 for $r$ and 0.509 for $p$. Furthermore, there is no essential difference among different choices of $T = 10^{-4}, 10^{-5}, 10^{-6}$. This is because $T$ is sufficiently small so that the error is dominated by the averaging error shown in Theorem 2. Also, since $T$ is very small, the $O(\varepsilon^{1/4} T^{1/2})$ term almost vanishes and we can only observe the half order convergence with respect to $\varepsilon$.

Then we fix $\gamma = 0.100$ and study the dependence on $T$ with $\varepsilon = 10^{-4}, 10^{-5}, 10^{-6}$. Figure 4.3 shows that when $T$ decreases, the errors of $r$ and $p$ decrease accordingly, until limited by the systematic error due to $\varepsilon$. The numerical order of convergence, estimated using the first five points with $\varepsilon = 10^{-6}$, is 0.964 for $r$ and 0.933 for $p$. In this case, $\varepsilon$ is small enough and we can only observe the $\varepsilon$-independent part of the contribution of the error as described in Theorem 3.

Our analysis indicates that the optimal strategy for choosing $\varepsilon$ and $T$ is that $T \sim \sqrt{\varepsilon}$. To confirm this, Figure 4.4 shows the errors with $\gamma = 0.100$ and $T = \sqrt{\varepsilon}$. 
Under such scaling, both $r$ and $p$ converges as $\varepsilon \to 0$. The order of convergence, estimated by data points with $\varepsilon \leq 2.00 \times 10^{-4}$, is 0.505 for $r$ and 0.506 for $p$. This yields excellent agreement with Theorem 1.

All the numerical convergence orders are collected in Table 4.1.
4.2. Efficiency. After establishing the accuracy of Stochastic-XLMD method, we demonstrate that with proper choice of parameters, Stochastic-XLMD indeed improves the efficiency by reducing the number of iterations for solving the nonlinear system (1.2b). This is the case for the polarizable force field model as proved in Theorem 1. However, numerical results indicate that the same behavior can also be observed for more general interaction energy that is non-quadratic with respect to \( x \) as well. In both cases, the interaction energy is nonlinear with respect to \( r \).

4.2.1. Polarizable force field model. Let \( r \in \mathbb{R}^3 \) and \( x \in \mathbb{R}^{20} \). Consider 
\[
F = -\partial U / \partial r \quad \text{with} \quad U = \frac{1}{4}|r|^4 + \frac{1}{100} \cos(400(r_1 + r_2 + r_3)).
\]
For the polarizable force field model, the non-zero entries in \( A \) are given by \( A_{k,k} = 2 + |r|^2, A_{k,k+1} = A_{k+1,k} = -1, A_{k,k+2} = A_{k+2,k} = (1-|r|^2)/2, b_k = \sin(kr/10 + (1-k/20)r_2 + r_3), k = 1, \ldots, 20 \). The choice of parameters are motivated from practical polarizable force field calculations, where the force \( F \) is strong and dominates the
fixed parameter variable & order for $r_\xi$ & order for $p_\xi$ \\ 
| $\gamma = 0.100, T = 10^{-9}$ | $\varepsilon$ | 0.402 & 0.509 \\
| $\gamma = 0.100, \varepsilon = 10^{-6}$ | $T$ | 0.964 & 0.933 \\
| $\gamma = 0.100$ | $\varepsilon, T = \sqrt{\varepsilon}$ | 0.505 & 0.506 \\

Table 4.1: Numerical convergence orders for $r_\xi$ and $p_\xi$.

| Method | Errors of $r$ | Errors of $p$ | Number of $Ax$ | Number of $(\partial_{x_k} A)x$ |
|---|---|---|---|---|
| MD | 0.0507 | 0.228 | 100392 | 37503 |
| Stochastic-XLMD | 0.0401 | 0.295 | 12518 | 37503 |

Table 4.2: Numerical errors and computational costs of MD and Stochastic-XLMD applied to the polarizable force field model.

dynamics at short time scale, while the interaction energy affects the dynamics at long time scale. The time interval is fixed to be $[0, 5]$. Initial values are $r(0) = (0, 0.500, 1.00)^T$, $p(0) = (1.00, 0.500, -1.00)^T$.

We compare numerical performance of MD (directly propagating MD (1.2)) and Stochastic-XLMD. For MD, we use the Verlet scheme to propagate the dynamics, and use the conjugate gradient method (CG) to solve the SCF iterations (i.e., solving the linear system). The reference solution is obtained with MD with a very small time step size $2.50 \times 10^{-6}$, and the SCF tolerance (measured in terms of the residue $|b - Ax|$) is set to $10^{-10}$. For Stochastic-XLMD, the BAOAB scheme is used for time propagation, and the time step size $1/2500$. Other parameters are chosen to be $\varepsilon = 5.00 \times 10^{-7}$, $T = \sqrt{\varepsilon}/1000$, $\gamma = 0.500$. In order to demonstrate the efficiency of Stochastic-XLMD, we perform MD simulation with the same time step size $1/2500$. The stopping criteria is set to be $10^{-6}$. We remark that such choice of tolerance is at the threshold, in the sense that the error of $p$ indeed increases if we set the tolerance to be larger. Such parameters are chosen such that all the dynamics are almost indistinguishable with the reference solution till $t = 3$ and remain reasonably accurate within the whole time interval. See Figure 4.5 for a comparison of $r$ and $p$ obtained by different methods.

Table 4.2 compares numerical errors and computational costs of MD and Stochastic-XLMD. Here the error in Stochastic-XLMD reported is computed by taking average of 10 independent simulations. The computational cost is measured by the number of matrix-vector multiplications. In each time step, the number of $Ax$ is equal to the number of SCF iterations plus one. We find that Stochastic-XLMD achieves similar accuracy compared to MD, but reduces the number of SCF iterations by 87.5%. After taking into account the matrix-vector multiplication operations due to $(\partial_{x_k} A)x$ for computing the force, Stochastic-XLMD still reduces the total matrix-vector multiplications by 63.7%.

4.2.2. **General interaction energy.** Next we test the effectiveness and efficiency of Stochastic-XLMD applied to a system with interaction energy $Q$ that is non-quadratic with respect to $x$. More specifically, we set

$$Q = \frac{1}{2} x^T A(r)x - x^T b(r) + 0.150 \left( |x|^2 + \frac{1}{2} \sum_{k=1}^{20} \sin(2x_k) \right).$$
Such choice of $Q$ will ensure that the Hessian matrix with respect to $x$ is uniformly positive definite, which means that the system of nonlinear equations

$$0 = -\frac{\partial Q}{\partial x}$$

has a unique solution and the dynamics is well-defined.

We use Anderson mixing without preconditioning [5] to solve the system of nonlinear equations, and all other numerical treatments remain to be the same. In Anderson mixing, the SCF tolerance is chosen to be $10^{-6}$. Such choice is again relatively tight, and further increase of the tolerance will increase the numerical errors in both $r$ and $p$. The mixing parameter $\alpha$ is set to be 0.100 to ensure convergence, and the mix-
The reference solution is obtained with very small time step size $2.50 \times 10^{-6}$. In the MD simulation, the time step size is chosen to be $1/2000$, while the time step size in Stochastic-XLMD is $1/2500$. Other parameters in Stochastic-XLMD are $\varepsilon = 2.50 \times 10^{-7}$, $T = \sqrt{\varepsilon}/10000$, $\gamma = 0.100$. Again, such parameters are chosen for all the dynamics to be almost indistinguishable with the reference solution till $t = 3.5$ and remain reasonably accurate within the whole time interval. See Figure 4.6 for a comparison of $r$ and $p$ obtained by different methods.

Table 4.3 compares numerical errors and computational costs of MD and Stochastic-XLMD. Here the error in Stochastic-XLMD reported is computed by taking average of 10 independent simulations. The computation cost is measured by the number of nonlinear evaluations, in particular, the number of evaluating $\partial Q/\partial x$. 

Fig. 4.6: Comparison of $r$ and $p$ obtained by MD and Stochastic-XLMD applied to the nonlinear example.
In each time step, this number is equal to the number of SCF iterations plus one. Similarly with the polarizable force field model, numerical errors of MD and Stochastic-XLMD are comparable, while 90.2% of nonlinear evaluations are reduced by using Stochastic-XLMD.

5. Conclusion. In this work, we consider a stochastic-extended Lagrangian molecular dynamics method, by introducing numerical fluctuation and dissipation through a Langevin type thermostat. For the polarizable force field model, with a suitable choice of the Lagrangian, we yield the Stochastic-XLMD method which generalizes the recently proposed iEL/0-SCF method [20, 4, 3]. We prove that the Stochastic-XLMD method converges to the accurate dynamics, and the convergence rate is sharp with respect to the singular perturbation parameter $\varepsilon$ and the numerical temperature $T$. We also analyze the impact of the damping factor in the Langevin dynamics and identify the optimal choice. While our analysis is done for the polarizable force field model, where the interaction energy is quadratic with respect to the latent degrees of freedom; under suitable conditions, our results can be generalized to accommodate more general interaction energy forms such as polynomials with higher degrees. Interesting future directions include theoretical understanding of the convergence of the Stochastic-XLMD scheme for other models such as the Kohn-Sham density functional theory, and the convergence of the original iEL/0-SCF scheme in the absence of noise. We also plan to study the numerical performance of Stochastic-XLMD for more realistic polarizable force field molecular dynamics simulations, and its comparison to other thermostat approaches such as the Nose-Hoover thermostat.

Acknowledgments. This work was partially supported by the National Science Foundation under grant DMS-1652330 (D.A. and L.L.) and DMS-1454939 (J.L.), by the Department of Energy under grant DE-SC0017867 (L.L.) and the U.S. Department of Energy, Office of Science, Office of Advanced Scientific Computing Research, Scientific Discovery through Advanced Computing (SciDAC) program (T.H.-G. and L.L.). We thank Christian Lubich, Anders Niklasson and Chao Yang for helpful discussions.

Appendix A. Proof of Proposition 6.
(a) Since $A$ is a positive definite matrix, there exist $\lambda_1 \geq \cdots \geq \lambda_d > 0$ and an orthonormal basis $\{v_k\}_{k=1}^d$ of $\mathbb{R}^d$ which satisfy
\[
A v_k = \lambda_k v_k, \quad k = 1, \cdots, d.
\]
Define
\[
\Upsilon = (\Upsilon_1, \cdots, \Upsilon_d) \in \mathbb{R}^{2d \times 2d}
\]
where
\[
\Upsilon_k = \frac{1}{\sqrt{2}} \begin{pmatrix} v_k & v_k \\ v_k & -v_k \end{pmatrix} \in \mathbb{R}^{2d \times 2}.
\]
It is easy to check \( U \) is an orthogonal matrix. Define

\[
\Upsilon^\top \mathcal{B} \Upsilon := J = \begin{pmatrix} J_{11} & \cdots & J_{1d} \\ \vdots & \ddots & \vdots \\ J_{d1} & \cdots & J_{dd} \end{pmatrix} \in \mathbb{R}^{2d \times 2d}
\]

with \( J_{kl} \in \mathbb{R}^{2 \times 2} \) given by

\[
J_{kl} = \Upsilon^\top_k \mathcal{B} \Upsilon_l = \frac{1}{2} \begin{pmatrix} v_k^\top v_l & -v_k^\top v_l \\ -v_k^\top v_l & v_k^\top v_l \end{pmatrix} \begin{pmatrix} 0 & -I_d \\ A & \gamma I_d \end{pmatrix} \begin{pmatrix} v_l & -v_l \\ v_l & v_l \end{pmatrix} = \frac{1}{2} \begin{pmatrix} v_k^\top A v_l + (\gamma - 1)v_k^\top v_l & v_k^\top A v_l + (1 - \gamma)v_k^\top v_l \\ -v_k^\top A v_l + (-1 - \gamma)v_k^\top v_l & -v_k^\top A v_l + (1 + \gamma)v_k^\top v_l \end{pmatrix}.
\]

Note that \( v_k^\top v_k = 1 \) and \( v_k^\top v_l = 0 \) if \( k \neq l \). Therefore \( J_{kl} = 0 \) if \( k \neq l \) and

\[
\Upsilon^\top \mathcal{B} \Upsilon = \begin{pmatrix} J_{11} & \cdots \\ \vdots \\ J_{dd} \end{pmatrix}
\]

with

\[
J_{kk} = \frac{1}{2} \begin{pmatrix} \lambda_k + \gamma - 1 & \lambda_k - \gamma + 1 \\ -\lambda_k - \gamma - 1 & -\lambda_k + \gamma + 1 \end{pmatrix}.
\]

Then we have

\[
\|e^{-B_t}\|_2 = \|\Upsilon^\top e^{-3t} \Upsilon\|_2 = \|e^{-3t}\|_2 = \max_{1 \leq k \leq d} \|\exp(-J_{kk}t)\|_2. \tag{A.1}
\]

Hence it is sufficient to find an upper bound for each \( \|\exp(-J_{kk}t)\|_2 \).

For notational simplicity, we will drop the subscript for \( J_{kk} \) and \( \lambda_k \), as the argument is identical for each \( k \). We have

\[
J^2 - \gamma J + \lambda I = 0, \tag{A.2}
\]

which can be obtained by noticing that \( x^2 - \gamma x + \lambda \) is the characteristic polynomial of \( J \) and applying Cayley-Hamilton Theorem. From Eq. (A.2) we have

\[
J^{n+2} = \gamma J^{n+1} - \lambda J^n, \quad \forall n. \tag{A.3}
\]

We now compute \( \exp(-Jt) \) explicitly using the above recursion relation. Define the roots of the characteristic polynomial to be

\[
\mu_{\pm} = \frac{\gamma \pm \sqrt{\gamma^2 - 4\lambda}}{2}.
\]

Note that \( \mu_{\pm} \) can be complex if \( \gamma^2 < 4\lambda \). We have

\[
J^{n+2} - \mu_+ J^{n+1} = \mu_- (J^{n+1} - \mu_+ J^n), \\
J^{n+2} - \mu_- J^{n+1} = \mu_+ (J^{n+1} - \mu_- J^n),
\]

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then
\[
J^{n+1} - \mu_+ J^n = \mu^n_+ (J - \mu_+ I),
\]
\[
J^{n+1} - \mu_- J^n = \mu^n_+ (J - \mu_- I).
\]
If \( \gamma^2 - 4\lambda \neq 0 \), then \( \mu_+ \neq \mu_- \) and we have
\[
J^n = \frac{1}{\mu_+ - \mu_-} \left[ \mu^n_+ (J - \mu_- I) - \mu^n_+ (J - \mu_+ I) \right].
\]

Then
\[
e^{-Jt} = \sum_{n=0}^{\infty} \frac{1}{n!} (-1)^n t^n J^n
\]
\[
= \frac{J - \mu_- I}{\mu_+ - \mu_-} \sum_{n=0}^{\infty} \frac{1}{n!} (-\mu_+ t)^n - \frac{J - \mu_+ I}{\mu_+ - \mu_-} \sum_{n=0}^{\infty} \frac{1}{n!} (-\mu_- t)^n
\]
\[
= \frac{J - \mu_+ I}{\mu_+ - \mu_-} e^{-\mu_+ t} - \frac{J - \mu_- I}{\mu_+ - \mu_-} e^{-\mu_- t}
\]
\[
= M^{(k)}_{\gamma} e^{-\delta^{(k)}_\gamma t},
\]
where
\[
\delta^{(k)}_\gamma = \begin{cases} 
\frac{\gamma}{2}, & 0 < \gamma \leq 2\sqrt{\lambda_k}, \\
(\gamma - \sqrt{\gamma^2 - 4\lambda_k})/2, & \gamma > 2\sqrt{\lambda_k}, 
\end{cases}
\]

and
\[
M^{(k)}_{\gamma} = \begin{cases} 
I \cos \left( \frac{\sqrt{2\lambda_k - \gamma^2}}{2} t \right) - \frac{2J_{kk} - \gamma I}{\sqrt{2\lambda_k - \gamma^2}} \sin \left( \frac{\sqrt{2\lambda_k - \gamma^2}}{2} t \right), & 0 < \gamma < 2\sqrt{\lambda_k}, \\
\left( 1 + \frac{\gamma^2}{4} \right) I + tJ_{kk}, & \gamma = 2\sqrt{\lambda_k}, \\
I + \frac{J_{kk} - \mu_- I}{\sqrt{\gamma^2 - 4\lambda_k}} \left[ \exp(-\sqrt{\gamma^2 - 4\lambda_k} t) - 1 \right], & \gamma > 2\sqrt{\lambda_k}.
\end{cases}
\]

The case \( \gamma = 2\sqrt{\lambda_k} \) can be obtained by taking the limit \( \gamma \to 2\sqrt{\lambda_k} \) from either side.

We now prove that there exists a constant \( C > 0 \) independent of \( \gamma \) and \( t \) such that
\[
\| M^{(k)}_{\gamma} e^{-\delta^{(k)}_\gamma t/2} \|_2 \leq C. \tag{A.7}
\]
In fact, if \( \gamma > 3\sqrt{\lambda_k} \), then \( \frac{J_{kk} - \mu_- I}{\sqrt{\gamma^2 - 4\lambda_k}} \) is bounded independently of \( \gamma \), and \( e^{-\sqrt{\gamma^2 - 4\lambda_k} t} \) is bounded by 1. Thus \( M^{(k)}_{\gamma} \) is bounded. If \( 0 < \gamma < \sqrt{\lambda_k} \), then by the fact that \( \frac{2J_{kk} - \gamma I}{\sqrt{\gamma^2 - 4\lambda_k}} \) is bounded independently of \( \gamma \), \( M^{(k)}_{\gamma} \) is also already bounded. Now we assume \( \sqrt{\lambda_k} \leq \gamma \leq 3\sqrt{\lambda_k} \), which means that \( \gamma, \delta^{(k)}_\gamma \) and \( 1/\delta^{(k)}_\gamma \) are all bounded so we can put all the \( \gamma \) dependence in the constant \( C \) and only focus on \( t \)-dependence. Using the fact that \( |\sin x/x| \) and \( |(e^{-x} - 1)/x| \) are both bounded by 1, and \( te^{-\delta^{(k)}_\gamma t} \) is also bounded, we can obtain the desired estimate in (A.7).

Finally, substitute Eq. (A.4) and estimate (A.7) into Eq. (A.1), we obtain
\[
\| e^{-2t} \|_2 = \max_{1 \leq k \leq d} \| \exp(-J_{kk} t) \|_2 \leq \max_{1 \leq k \leq d} C e^{-\delta^{(k)}_\gamma t/2} \leq C e^{-\delta_\gamma t},
\]

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(b) According to Eq. (3.3)

\[
\|S_t - S_\infty\|_2 \leq C\gamma T \int_t^\infty \|e^{-B_s}\|_2 \|e^{-B^{\top}_s}\|_2 ds
\]

\[
\leq C\gamma T \int_t^\infty e^{-2\delta_s t} ds
\]

\[
\leq C\frac{\gamma}{\delta_t} T e^{-2\delta_s t}.
\]

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