

# CLASSICAL LANGEVIN DYNAMICS DERIVED FROM QUANTUM MECHANICS

HÅKON HOEL

Chair of Mathematics for Uncertainty Quantification  
RWTH Aachen University  
Germany

ANDERS SZEPESSY\*

Institutionen för Matematik  
Kungl. Tekniska Högskolan  
100 44 Stockholm, Sweden

ABSTRACT. The classical work by Zwanzig [J. Stat. Phys. 9 (1973) 215-220] derived Langevin dynamics from a Hamiltonian system of a heavy particle coupled to a heat bath. This work extends Zwanzig's model to a quantum system and formulates a more general coupling between a particle system and a heat bath. The main result proves, for a particular heat bath model, that *ab initio* Langevin molecular dynamics, with a certain rank one friction matrix determined by the coupling, approximates for any temperature canonical quantum observables, based on the system coordinates, more accurately than any Hamiltonian system in these coordinates, for large mass ratio between the system and the heat bath nuclei.

## 1. LANGEVIN MOLECULAR DYNAMICS

Langevin dynamics for (unit mass) particle systems with position coordinates  $X_L : [0, \infty) \rightarrow \mathbb{R}^N$  and momentum coordinates  $P_L : [0, \infty) \rightarrow \mathbb{R}^N$ , defined by

$$(1) \quad \begin{aligned} dX_L(t) &= P_L(t)dt \\ dP_L(t) &= -\nabla\lambda(X_L(t))dt - \bar{\kappa}P_L(t)dt + (2\bar{\kappa}T)^{1/2} dW(t), \end{aligned}$$

is used for instance to simulate molecular dynamics in the canonical ensemble of constant temperature  $T$ , volume and number of particles, where  $W$  denotes the standard Wiener process with  $N$  independent components. The purpose of this work is to precisely determine both the potential  $\lambda : \mathbb{R}^N \rightarrow \mathbb{R}$  and the friction matrix  $\bar{\kappa} \in \mathbb{R}^{N \times N}$  in this equation, from a quantum mechanical model of a molecular system including weak coupling to a heat bath.

Molecular systems are described by the Schrödinger equation with a potential based on Coulomb interaction of all nuclei and electrons in the system. This quantum mechanical model is complete in the sense that no unknown parameters enter - the observables in the canonical ensemble are determined from the Hamiltonian and the temperature. The classical limit of the quantum formulation, yields an accurate

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\* Corresponding author: Anders Szepessy (szepessy@kth.se).

approximation of the observables based on the nuclei only, for large nuclei–electron mass ratio  $M$ . Ab initio molecular dynamics based on the electron ground state eigenvalue can be used when the temperature is low compared to the first electron eigenvalue gap. A certain weighted average of different ab initio dynamics, corresponding to each electron eigenvalue, approximates quantum observables for any temperature, see [10], also in the case of observables including time correlation and many particles. The elimination of the electrons provides a substantial computational reduction, making it possible to simulate large molecular systems, cf. [18].

In molecular dynamics simulations one often wants to determine properties of a large macroscopic system with many particles, say  $N \sim 10^{23}$ . Such large particle systems cannot yet be simulated on a computer and one may then ask for a setting where a smaller system has similar properties as the large. Therefore, we seek an equilibrium density that has the property that the marginal distribution for a subsystem has the same density as the whole system. In [10] it is motivated how this assumption leads to the Gibbs measure, i.e. the canonical ensemble; this is also the motivation to use the canonical ensemble for the composite system in this work, although some studies on heat bath models use the microcanonical ensemble for the composite whole system.

Langevin dynamics is often introduced to sample initial configurations from the Gibbs distribution and to avoid to simulate the dynamics of all heat bath particles. The friction/damping parameter in the Langevin equation is then typically set small enough to not perturb the dynamics too much and large enough to avoid long sampling times.

The purpose of this work is to show that Langevin molecular dynamics, for the non heat bath nuclei, with a certain friction/damping parameter determined from the Hamiltonian, approximates the quantum system, in the canonical ensemble for any temperature, more accurately than any Hamiltonian dynamics (for the non heat bath particles) in the case the system is weakly coupled to a heat bath of many fast particles.

Our heat bath model is based on the assumption of weak coupling - in the sense that the perturbation in the system from the heat bath is small and vice versa - which we show leads to Zwanzig’s model for nonlinear generalized Langevin equations in [28], with a harmonic oscillator heat bath. Zwanzig also derives a pure Langevin equation: he assumes first a continuous Debye distribution of the eigenvalues of the heat bath potential energy quadratic form; in the next step he lets the coupling to the heat bath have a special form, so that the integral kernel for the friction term in the generalized Langevin equation becomes a Dirac-delta measure. Our derivation uses a heat bath based on nearest neighbour interaction on an infinite cubic lattice, so that the continuum distribution of eigenvalues is rigorously obtained by considering a difference operator with an infinite number of nodes. Our convergence towards a pure Langevin equation is not based on a Dirac-delta measure for the integral kernel but obtained from the time scale separation of the fast heat bath particles and the slower system particles, which allows a general coupling and a bounded covariance matrix for the fluctuations. The fast heat bath dynamics is provided either from light heat bath particles or a stiff heat bath potential. By a stiff heat bath we mean that the smallest eigenvalue of the Hessian of the heat bath potential energy is of the order  $\chi^{-1}$ , where  $\chi \ll 1$ . We show that the friction/damping coefficient in the pure Langevin equation is determined

by the derivative of the forces on the heat bath particles with respect to the system particle positions. We also prove that the observables of the system coordinates in the system-heat bath quantum model can be approximated using this Langevin dynamics with accuracy  $\mathcal{O}(m \log m^{-1} + (mM)^{-1})$ , where  $M \gg 1$  is the system nuclei–electron mass ratio and  $m \ll 1$  is the heat bath nuclei – system nuclei mass ratio; the approximation by a Hamiltonian system yields the corresponding larger error estimate  $\mathcal{O}(m^{1/2} + (mM)^{-1})$ , in the case of light heat bath particles. In this sense, our Langevin equation is a better approximation. The case with a stiff heat bath system has the analogous error estimate  $\mathcal{O}(\chi^{2\delta} \log \chi^{-1} + M^{-1})$  with the correct friction/damping parameter, while a Hamiltonian system gives the larger error  $\mathcal{O}(\chi^{2\delta-1/2} + M^{-1})$ , where  $\chi^\delta \ll \chi^{1/4}$  measures the coupling between the heat bath and the system. Our main assumptions are:

- the coupling between the system and the heat bath is weak and localized,
- either the heat bath particles are much lighter than the system particles or the heat bath is stiff,
- the harmonic oscillator heat bath is constructed from nearest neighbour interaction on an infinite cubic lattice in dimension three,
- the heat bath particles are initially randomly Gibbs distributed (conditioned by the system particle coordinates), and
- the system potential energy and the observables are sufficiently regular.

The system and the heat bath is modelled by a Hamiltonian where the system potential energy is perturbed by  $\bar{V}(x, X)$  with system particle positions  $X \in \mathbb{R}^N$  and heat bath particle positions  $x \in \mathbb{R}^n$ . Our assumption of weak coupling is formulated as the requirement that the potential  $\bar{V}$  satisfies

$$\min_{x \in \mathbb{R}^n} \bar{V}(x, X) = \bar{V}(a(X), X) = 0.$$

Theorem 3.4 proves that the obtained minimizer  $a(X) \in \mathbb{R}^n$  determines the friction matrix  $\bar{\kappa}$  in (1) by the rank one  $N \times N$  matrix

$$(2) \quad \bar{\kappa}_{\ell\ell'} = \bar{c} m^{1/2} \langle \bar{V}''(a, X) \partial_{X_\ell} a, \bar{V}''(a, X) \partial_{X_{\ell'}} a \rangle,$$

where  $\bar{V}$  and  $a$  have limits as  $n \rightarrow \infty$ ; here  $\bar{V}''$  denotes the Hessian of  $\bar{V}$  with respect to  $x$ , the brackets  $\langle \cdot, \cdot \rangle$  denote the scalar product in  $\mathbb{R}^n$  and  $\bar{c}$  is a constant (related to the density of states).

In a setting when the temperature is small compared to the difference of the two smallest eigenvalues of the Hamiltonian symbol, with given nuclei coordinates, it is well known that ab initio molecular dynamics is based on the ground state electron eigenvalue as the potential  $\lambda$  in (1), cf. [18]. When the temperature is larger, excited electron states influence the nuclei dynamics. The work [10] derives a molecular dynamics approximation of quantum observables, including time correlations, as a certain weighted average of ab initio observables in the excited states, and these ideas are put into the context of this work in Section 5.

The analysis of particles in a heat bath has a long history, starting with the work by Einstein and Smoluchowski. The Langevin equation was introduced in [14] to study Brownian motion mathematically, before the Wiener process was available. Early results on the elimination of the heat bath degrees of freedom to obtain a Langevin equation are [7, 6] and [28],[27, Section 9.3]. The work [7, 6] include in addition a derivation of a quantum Langevin equation, which is based on an operator version of the classical Langevin equation. Our study of the classical Langevin equation from quantum mechanics is not related to this quantum Langevin

equation. We start with an ab initio quantum model of the system coupled to a heat bath in the canonical ensemble and use its classical limit to eliminate the electron degrees of freedom. Then the classical system coupled to the heat bath is analyzed by separation of time scales. The separation of time scales of light bath particles and heavier system particles was first used in [15], see also [20, 23] to determine a Fokker-Planck equation for the system particle, from the Liouville equation of the coupled system using a formal expansion in the small mass ratio. Section 8 in [22] presents a proof, and several references to related work, where the Langevin equation is derived from the generalized Langevin equation, using exponential decay of the kernel in the memory term of the generalized Langevin equation.

Our contribution employs the separation of time scales approach previously used in [15, 20, 23], but a novelty is that we here present mathematical proofs for the weak convergence rate of Langevin dynamics towards quantum mechanics. Our work also differs from [22, Section 8], wherein the kernel of the generalized Langevin equation is assumed to be such that by adding a finite dimensional variable the system becomes Markovian and the kernel tends to a point mass. For instance, our kernel vanishes as  $m \rightarrow 0^+$  and we use the density of heat bath states to determine the kernel. Using the precise information from the density of states in the case of heat bath nearest neighbor interaction in a cubic lattice we obtain a positive definite friction matrix  $\bar{\kappa}$ , while if the nearest neighbor interaction would be related to a lattice in dimension four the friction matrix would vanish, see Remark 4.

The main new ideas in our work are the first principles formulation from quantum mechanics, the weak coupling condition as a minimization, the precise use of the density of heat bath states, that the error estimate uses stability of the Kolmogorov backward equation for the Langevin equation evaluated along the dynamics of the coupled system, and formulation of numerical schemes and numerical results related to Langevin dynamics approximation of particles systems.

Although our heat bath formulation starts from a quantum mechanical description, our analysis impose restrictions on the generality. In a first step the classical limit of a quantum system and heat bath interaction is derived by semi-classical analysis in Section 5 and the classical interaction potential is approximated by pair interactions in Section 3.1.1. The finally result is proved based on an example of pair interactions. Therefore the main limitation in our work is the analysis restriction to a harmonic oscillator heat bath model based on nearest neighbour interaction on periodic cubic lattices, with  $n$  points. The use of the restrictive heat bath model here is due to the mathematical techniques in the convergence analysis. The analysis impose in particular four additional conditions for the interaction potential  $\bar{V}(x, X)$ , namely

**Assumption 1.1.** The Hessian matrix  $\bar{V}''$  in (2) is constant, i.e. we use a harmonic oscillator approximation as motivated in (4).

**Assumption 1.2.** The classical force on each heat bath particle  $j$  has a constant derivative  $F'_{\ell j} = (\bar{V}'' \partial_{\ell} a(X))_j$  with respect to each system particle position  $X_{\ell}$ , see (11) and (13).

**Assumption 1.3.** The force derivative  $F'_{\ell j}$  is localized, in the sense that for a fixed system particle  $\ell$ , the force derivative decays with a certain rate with respect  $j$  as measured by the distance between the heat bath particle  $j$  and the system particle  $\ell$ , see (13).

**Assumption 1.4.** The potentials for different number of lattice points  $n$  are related so that the force derivative  $F'_{\ell_j}$  has a limit as the number of lattice points  $n$  tends to infinity, see (13).

General heat bath models could also satisfy assumptions 1.3 and 1.4 while assumptions 1.1 and 1.2 would typically not hold exactly but may be local approximations, as motivated in Section 3.1.1.

Section 2 formulates a classical model for the system and the heat bath, including the weak coupling, and derives the corresponding generalized Langevin equation, based on a memory term with a specific integral kernel, in a classical molecular dynamics setting. The generalized Langevin equation is analyzed in Section 3, with subsections related to the dissipation, fluctuations and approximation by pure Langevin dynamics in the case of light heat bath particles. The main result of Section 3 is Theorem 3.4, where a certain Langevin dynamics is shown to approximate a classical system weakly coupled to a heat bath. Section 4 extends the analysis to the case of stiff heat baths and derives a corresponding approximation result in Theorem 4.1. Section 5 relates the classical model to a quantum formulation and provides background and error estimates on quantum observables in the canonical ensemble approximated by classical molecular dynamics. The main result of the work is Theorem 5.2, which proves that for any temperature canonical quantum observables based on the system coordinates can be accurately approximates by the Langevin dynamics obtained in Theorems 3.4 and 4.1. Section 6 includes numerical results of the system particle density and autocorrelation of the coupled system and heat bath approximated by the particle density and autocorrelation for the Langevin dynamics. The aim of the numerical examples is to show for a simple model problem that the classical system coupled to the heat bath model, described by a generalized Langevin equation, is well approximated by the derived Langevin equation as the mass ratio of heat bath and system particles vanish. The important comparison of the derived Langevin equation to experiments based on real matter remains for future work.

## 2. THE MODEL OF THE SYSTEM AND THE HEAT BATH

We consider in this section a classical model of a molecular system, with position coordinates  $X \in \mathbb{R}^N$  and momentum coordinates  $P \in \mathbb{R}^N$ , coupled to a heat bath, with position and momentum coordinates  $x \in \mathbb{R}^n$  and  $p \in \mathbb{R}^n$ , respectively, represented by the Hamiltonian

$$\frac{|P|^2}{2} + \frac{|p|^2}{2m} + \lambda(X) + \bar{V}(x, X),$$

where  $\lambda : \mathbb{R}^N \rightarrow \mathbb{R}$  is the potential energy for the system and  $\bar{V} : \mathbb{R}^n \times \mathbb{R}^N \rightarrow \mathbb{R}$  is the potential energy for the heat bath including the coupling to the system. The parameter  $m$  is the mass ratio between heat bath nuclei and system nuclei. We have set the time scale so that the system nuclei mass is one. In Section 5 we show that this model is the classical limit of a quantum model and study the accuracy of the classical approximation, also in the case with system nuclei that have different masses.

We study small perturbations of the equilibrium bath state  $x = a(X) \in \mathbb{R}^n$  where

$$\min_{x \in \mathbb{R}^n} \bar{V}(x, X) = \bar{V}(a(X), X).$$

Taylor expansion around the equilibrium yields

$$\bar{V}(x, X) = \bar{V}(a(X), X) + \frac{1}{2} \langle x - a(X), \bar{V}_{xx}''(a(X) + \xi(x - a(X)), X)(x - a(X)) \rangle$$

for some  $\xi \in [0, 1]$  depending on  $(x, X)$ , where  $\bar{V}_{xx}$  is the Hessian matrix in  $\mathbb{R}^{n \times n}$ , with respect to the  $x$  coordinate, and the notation  $\langle \cdot, \cdot \rangle$  is the standard scalar product in  $\mathbb{C}^n$ . We assume that the coupling between the system and the heat bath is weak, which means that the perturbation in the system from the heat bath must be small. As the perturbation  $|x - a(X)| \rightarrow 0$  we therefore require that

$$(3) \quad \bar{V}(a(X), X) = 0.$$

Weak coupling also means that the perturbation in the heat bath from the system is small, so that the influence on the Hessian  $\bar{V}_{xx}''$  from  $X$  is negligible, and we assume following Assumption 1.1 therefore that

$$(4) \quad \bar{V}_{xx}''(a(X) + \xi(x - a), X) = C$$

where  $C$  is constant, symmetric and positive definite. Hence the vibration frequencies for  $x$  are assumed to be constant for all  $x$  and  $X$ . We use the notation  $C = \bar{V}''$  below.

The assumptions (3) and (4) of weak coupling lead to the Hamiltonian  $H : \mathbb{R}^N \times \mathbb{R}^N \times \mathbb{R}^n \times \mathbb{R}^n \rightarrow \mathbb{R}$

$$(5) \quad H(X, P, x, p) = \frac{|P|^2}{2} + \frac{|p|^2}{2m} + \lambda(X) + \frac{1}{2} \langle \bar{V}''(x - a(X)), x - a(X) \rangle.$$

This model (5) is of the same form as the model of interaction with a heat bath introduced and analysed by Zwanzig in the seminal work [28], although here the motivation with weak coupling and several system particles is different.

The Hamiltonian (5) yields the dynamics

$$\begin{aligned} \dot{X}_t &= P_t \\ \dot{P}_t &= -\nabla \lambda(X_t) + \langle \bar{V}''(x_t - a(X_t)), \nabla a(X_t) \rangle \\ \dot{x}_t &= p_t/m \\ \dot{p}_t &= -\bar{V}''(x_t - a(X_t)) \end{aligned}$$

and the change of variables  $(m\bar{V}'')^{1/2}r_t := p_t$  implies

$$\begin{aligned} \dot{x}_t &= m^{-1/2} \bar{V}''^{1/2} r_t \\ \dot{r}_t &= -m^{-1/2} \bar{V}''^{1/2} (x_t - a(X_t)). \end{aligned}$$

Define  $\varphi_t := x_t - a(X_t) + ir_t$  to obtain

$$(6) \quad \begin{aligned} \dot{X}_t &= P_t \\ \dot{P}_t &= -\nabla \lambda(X_t) + \operatorname{Re} \langle \bar{V}'' \varphi_t, \nabla a(X_t) \rangle \\ i\dot{\varphi}_t &= m^{-1/2} \bar{V}''^{1/2} \varphi_t - i\dot{X}_t \cdot \nabla a(X_t), \end{aligned}$$

where the third equation uses the notation  $v \cdot w$  for the standard scalar product in  $\mathbb{R}^N$ .

Assume that  $x_0$  and  $p_0$  are Gaussian with the distributions provided by the marginals of the Gibbs density

$$\frac{e^{-H(X,P,x,p)/T}}{\int_{\mathbb{R}^{2N+2n}} e^{-H(X,P,x,p)/T} dX dP dx dp},$$

that is, the momentum  $p$  is multivariate normal distributed with mean zero and covariance matrix  $mTI$  and independent of  $x$ , which is multivariate normal distributed with mean  $a(X)$  and covariance matrix  $T(\bar{V}'')^{-1}$ . Consequently the initial data can be written

$$(7) \quad \varphi_0 = \sum_{k=1}^n \gamma_k \nu'_k$$

using the orthogonal eigenvectors  $\nu'_m$ , normalized as  $\langle \nu'_k, \nu'_k \rangle = 1$ , and eigenvalues  $\mu_m$  of  $\bar{V}''$

$$(8) \quad \bar{V}'' \nu'_m = \mu_m \nu'_m, \quad \nu'_m \in \mathbb{R}^n \text{ and } \mu_m \in \mathbb{R}_+$$

and the definition

$$(9) \quad \gamma_m := \gamma_m^r + i\gamma_m^i$$

with  $\gamma_m^r$  and  $\gamma_m^i$ ,  $m = 1, \dots, n$ , independent and normal distributed real scalar random numbers with mean zero and variance  $T/\mu_m$ .

Duhamel's principle shows that

$$\varphi_t = e^{-i\bar{V}''^{1/2} m^{-1/2} t} \varphi_0 - \int_0^t e^{-i\bar{V}''^{1/2} m^{-1/2} (t-s)} \dot{a}(X_s) ds$$

which implies a form of Zwanzig's generalized Langevin equation

$$(10) \quad \begin{aligned} \ddot{X}_t &= -\nabla\lambda(X_t) - \int_0^t \langle \bar{V}'' \cos\left(\frac{(t-s)\bar{V}''^{1/2}}{m^{1/2}}\right) \dot{a}(X_s), \nabla a(X_t) \rangle ds \\ &\quad + \text{Re}\langle \bar{V}'' e^{-i\bar{V}''^{1/2} m^{-1/2} t} \varphi_0, \nabla a(X_t) \rangle, \end{aligned}$$

with non Markovian friction term given by the integral and a noise term including the stochastic initial data  $\varphi_0$ . We study two different cases:

- either the mass ratio  $m \ll 1$  is small, or
- the smallest eigenvalue of  $\bar{V}''$  is large of the order  $\chi^{-1}$  while the coupling derivative  $\|\nabla a\|$  is small of size  $\chi^\delta$  with  $\delta > 1/4$ .

In these cases, both the friction and the noise terms are based on highly oscillatory functions, which will make these contributions small, as explained in the next section. To simplify the analysis we assume that Assumptions 1.1 and 1.2 hold, which imply that

$$(11) \quad \nabla a(\cdot) \text{ is a constant matrix,}$$

since the matrices  $\bar{V}''$  and  $F'$  are constant,  $\bar{V}''$  is non singular and  $F' = \bar{V}'' \nabla a(X)$ .

### 3. ANALYSIS OF THE GENERALIZED LANGEVIN EQUATION FOR $m \ll 1$

In this section we first study the dissipation term  $\int_0^t \langle \bar{V}'' \cos\left(\frac{(t-s)\bar{V}''^{1/2}}{m^{1/2}}\right) \dot{a}(X_s), \nabla a \rangle ds$  and the fluctuation term  $\text{Re}\langle \bar{V}'' e^{-i\bar{V}''^{1/2} m^{-1/2} t} \varphi_0, \nabla a \rangle$  in (10), as the number of bath particles tend to infinity and the mass ratio,  $m$ , between light heat bath nuclei and heavier system nuclei is small. Then in Section 3.3 we prove an a priori estimate of  $\sup_{s < t} \mathbb{E}[|X_s|^2 + |\dot{X}_s|^2 + |\ddot{X}_s|^2]$ . Section 3.4 uses the limit terms to construct a Langevin equation, namely the Itô stochastic differential equation

$$(12) \quad \begin{aligned} dX_L(t) &= P_L(t) dt \\ dP_L(t) &= -\nabla\lambda(X_L(t)) dt - m^{1/2} \kappa P_L(t) dt + (2m^{1/2} \kappa T)^{1/2} dW(t), \end{aligned}$$

with a certain symmetric friction matrix  $\kappa \in \mathbb{R}^{N \times N}$  and a Wiener process  $W : [0, \infty) \times \Omega \rightarrow \mathbb{R}^N$ , with  $N$  independent components; here  $\Omega$  is the set of outcomes for the process  $(X, P) : [0, \infty) \times \Omega \rightarrow \mathbb{R}^{2N}$ . Finally, we use the solution of the Kolmogorov backward equation for the Langevin dynamics along a solution path  $(X_t, P_t)$  of (10) to derive an error estimate of the approximation, namely  $\mathbb{E}[g(X_t, P_t)] - \mathbb{E}[g(X_L(t), P_L(t))] = \mathcal{O}(m \log m^{-1})$ , for any given smooth bounded observable  $g : \mathbb{R}^{2N} \rightarrow \mathbb{R}$  and equal initial data  $(X(0), P(0)) = (X_L(0), P_L(0))$ .

**3.1. The dissipation term and a precise heat bath.** The change of variables

$$\frac{t-s}{m^{1/2}} = \tau$$

yields

$$\begin{aligned} & \int_0^t \langle \bar{V}'' \cos\left(\frac{(t-s)V''^{1/2}}{m^{1/2}}\right) \dot{a}(X_s), \partial_{X^\ell} a \rangle ds \\ &= m^{1/2} \int_0^{t/\sqrt{m}} \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \dot{a}(X_{t-m^{1/2}\tau}), \partial_{X^\ell} a \rangle d\tau \\ &= \sum_{\ell'} m^{1/2} \int_0^{t/\sqrt{m}} \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \partial_{X^{\ell'}} a, \partial_{X^\ell} a \rangle \dot{X}_{t-\sqrt{m}\tau}^{\ell'} d\tau. \end{aligned}$$

We require this dissipation term to be small, so that the coupling to the heat bath yields a small perturbation of the dynamics for  $X$  and  $P$ . If  $\bar{V}''$  and  $\nabla a$  are of order one, the mass  $m$  needs to be small, or if  $\nabla a$  is small we can have  $\bar{V}''$  large. The case with small  $m$  is studied in this section and the case with large  $\bar{V}''$  is in Section 4.

A small mass also requires the integrand to decay as  $\tau \rightarrow \infty$ . We will use Fourier analysis to study the decay of the kernel

$$K_n^{\ell\ell'} := \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \partial_{X^{\ell'}} a, \partial_{X^\ell} a \rangle,$$

by writing  $\lim_{n \rightarrow \infty} K_n$  as an integral, which is the next step in the analysis.

The kernel  $K_n$  is based on the equilibrium heat bath position derivative  $\partial_{X^\ell} a$  and this derivative is determined by the derivative of the force on bath particle  $x_j$ , with respect to  $X^\ell$ , by (5) as

$$F'_{\ell,j} := -\partial_{X^\ell} \partial_{x_j} \bar{V}(x, X) = (\bar{V}'' \partial_{X^\ell} a)_j,$$

which, for fixed  $\ell$  and  $j$ , by assumptions (4) and (11) is independent of  $x$  and  $X$ . We assume that Assumptions 1.3 and 1.4 hold, and more precisely that  $\bar{V}$  is constructed so that this force derivative is localized in the sense

$$(13) \quad \sum_j |F'_{\ell,j}| (1 + |j - \hat{\ell}|^2) = \mathcal{O}(1), \quad \text{as } n \rightarrow \infty, \text{ for } \hat{\ell} := \operatorname{argmin}_j |X_\ell - x_j|$$

$\lim_{n \rightarrow \infty} F'_{\ell,j}$  exists.

Let  $\nu_k(j) := \nu'_k(j) / \max_j |\nu'_k(j)|$  be the set of orthogonal eigenvectors of  $\bar{V}''$  that are normalized to one in the maximum norm. The eigenvalue representation of  $\bar{V}''$  in (8) and the definition

$$\omega_k^2 = \mu_k$$



yields

$$\begin{aligned}
 \beta_{\ell,k} &:= \sum_j F'_{\ell,j} \nu_k^*(j) = \langle \nu_k, F'_{\ell} \rangle, \\
 F'_{\ell,j} &= (\bar{V}'' \partial_{X^\ell} a)_j = \sum_k \frac{\beta_{\ell,k}}{\|\nu_k\|_2^2} \nu_k(j), \\
 \partial_{X^\ell} a_j &= \sum_k \frac{\beta_{\ell,k}}{\omega_k^2 \|\nu_k\|_2^2} \nu_k(j),
 \end{aligned}
 \tag{14}$$

where  $\|\nu_k\|_2 := (\sum_j |\nu_k(j)|^2)^{1/2}$ . Consequently we obtain

$$\begin{aligned}
 K_n^{\ell\ell'}(\tau) &= \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \partial_{X^\ell} a, \partial_{X^{\ell'}} a \rangle \\
 &= \sum_k \cos(\tau \omega_k) \frac{\beta_{\ell,k}^* \beta_{\ell',k}}{\omega_k^2 \|\nu_k\|_2^2}.
 \end{aligned}
 \tag{15}$$

If  $n$  is finite and we make a tiny perturbation of  $\bar{V}''$  so that all  $\omega_k$  become rational, the function  $K_n$  will be periodic in  $\tau$  and consequently it will not decay for large  $\tau$ . To obtain a decaying kernel we will therefore consider a heat bath with infinite number of particles,  $n = \infty$ , which requires a more precise formulation of the heat bath. The next section presents heat bath models based on pair interactions and motivates the related Assumptions 1.1-1.4 on  $\bar{V}$ . Then in Section 3.1.2 a particular simple pair interaction model is formulated to study the limit of  $K_n$ , as  $n \rightarrow \infty$ .

**3.1.1. Motivation for Assumptions 1.1-1.4.** To provide a motivation for Assumptions 1.1-1.4 of the heat bath potential  $\bar{V}$ , consider a classical heat bath model based on pair interactions with one system particle  $X = x_1 \in \mathbb{R}^3$  and  $n' - 1 = n/3$  heat bath particles  $x = (x_2, \dots, x_{n'}) \in \mathbb{R}^{3(n'-1)}$

$$\bar{V}(x, X) = \frac{1}{2} \sum_{i=1}^{n'} \sum_{j=1}^{n'} \phi(|x_i - x_j|).$$

Let for instance  $\phi$  be a Lennard-Jones potential  $\phi(r) = 4\epsilon((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6)$ , which for given positive constants  $\epsilon$  and  $\sigma$  model noble gases, see [26]. The force on particle  $j$  becomes

$$-\nabla_{x_j} \bar{V}(x, X) = -\sum_{i \neq j} \nabla_{x_j} \phi(|x_j - x_i|)$$

and the force gradient with respect to  $X = x_1$  is

$$f'_{1j} = -\partial_X \partial_{x_j} \bar{V}(x, X) = -\partial_{x_1} \partial_{x_j} \phi(|x_j - x_1|).
 \tag{16}$$

We have

$$\min_x \bar{V}(x, X) = \bar{V}(a(X), X)$$

where  $a_j(X)$ ,  $j = 1, \dots, n'$  form a face-centered-cubic lattice including also the point  $a_1(X) = X = x_1$ , see [26]. By considering small values of  $|x_j - a_j|$  compared to  $|a_j - a_i|$ , for  $j \neq i$ , we obtain the harmonic oscillator approximation

$$\bar{V}(x, X) \simeq \bar{V}(a(X), X) + \frac{1}{2} \langle x - a(X), \bar{V}''(x - a(X)) \rangle,
 \tag{17}$$

where

$$\begin{aligned} \bar{V}_{ij}'' &:= (\bar{V}_{xx}''(a(X), X))_{ij} = \\ &\begin{cases} \sum_{k \neq j} \left( \phi''(|a_j - a_k|) \frac{a_j - a_k}{|a_j - a_k|} \otimes \frac{a_j - a_k}{|a_j - a_k|} - \frac{\phi'(|a_j - a_k|)}{|a_j - a_k|} \left( \frac{a_j - a_k}{|a_j - a_k|} \otimes \frac{a_j - a_k}{|a_j - a_k|} - \mathbb{I} \right) \right), & i = j, \\ -\phi''(|a_j - a_i|) \frac{a_j - a_i}{|a_j - a_i|} \otimes \frac{a_j - a_i}{|a_j - a_i|} + \frac{\phi'(|a_j - a_i|)}{|a_j - a_i|} \left( \frac{a_j - a_i}{|a_j - a_i|} \otimes \frac{a_j - a_i}{|a_j - a_i|} - \mathbb{I} \right), & i \neq j. \end{cases} \end{aligned}$$

Here the distances between lattice points,  $|a_j - a_i|$ , are at least of the order one while (6) and Lemma 3.3 show that in our heat bath model with constant  $\bar{V}''$  we have  $|x_j - a_j|$  small compared to one, if the temperature  $T$  and mass  $m$  both are small compared to one. Therefore the assumption that  $|x_j - a_j|$  is small compared to  $|a_j - a_i|$  is consistent with the study here. The constant force derivative approximation is then by (16) related to the harmonic oscillator approximation and becomes

$$f'_{1j} \simeq -\bar{V}_{1j}'' =: F'_{1j}, \quad j = 2, \dots, n'.$$

which is localized due to the decay of  $\phi$ . Relating to the constraints (13), we note for this particular model problem that since  $\bar{V}_{1j}''$  is constant and independent of  $n'$ , it follows that  $\lim_{n \rightarrow \infty} F'_{1j}$  exists and that

$$\sum_j |F'_{1,j}| (1 + |j - \hat{\ell}|^2) = \mathcal{O} \left( \int_1^\infty |\phi''(r)| (1 + r^2) r^2 dr \right) = \mathcal{O}(1).$$

In conclusion a heat bath model based on pair interactions with a sufficiently localized potential  $\phi$  provides a motivation for Assumptions 1.1-1.4. The model can directly be extended to several system particles and different pair interactions for heat bath and system particles, so that

$$\begin{aligned} F'_{\ell j} &= -(\bar{V}'' \partial_{X^\ell} a)_j \\ &= \phi_\ell''(|a_j - a_\ell|) \frac{a_j - a_\ell}{|a_j - a_\ell|} \otimes \frac{a_j - a_\ell}{|a_j - a_\ell|} - \frac{\phi_\ell'(|a_j - a_\ell|)}{|a_j - a_\ell|} \left( \frac{a_j - a_\ell}{|a_j - a_\ell|} \otimes \frac{a_j - a_\ell}{|a_j - a_\ell|} - \mathbb{I} \right), \end{aligned}$$

which determines the constant matrix  $\nabla a$ . Here  $\phi_\ell$  is the interaction potential between system particle  $\ell$  and heat bath particle  $j$ .

3.1.2. *A precise heat bath.* To study  $\lim_{n \rightarrow \infty} K_n$  we choose an example of a heat bath model (17) where the equilibrium points  $a_j$  form a cubic lattice and the interactions are limited to the nearest neighbor lattice points, namely we use the periodic lattice

$$E_{\bar{n}} := \{-\bar{n}/2, -\bar{n}/2 + 1, \dots, \bar{n}/2 - 1\}^3 \subset \mathbb{R}^3$$

in dimension three to form the equilibrium positions for the heat bath. The position deviation from the equilibrium, namely  $\bar{x}_j := x_j - a_j(X) \in \mathbb{R}$  for each particle  $j \in E_{\bar{n}}$ , is then determined by the potential by nearest neighbour interaction in the lattice

$$\begin{aligned} \langle \bar{V}'' \bar{x}, \bar{x} \rangle &= c^2 \sum_{i=1}^3 \sum_{j \in E_{\bar{n}}} |\bar{x}_{j+e_i} - \bar{x}_j|^2 + \eta_n^2 \sum_{i=1}^3 \sum_{j \in E_{\bar{n}}} |\bar{x}_{j+e_i}|^2 \\ (18) \quad &= c^2 \sum_{i=1}^3 \sum_{j \in E_{\bar{n}}} (-\bar{x}_{j+e_i} + 2\bar{x}_j - \bar{x}_{j-e_i}) \bar{x}_j + \eta_n^2 \sum_{i=1}^3 \sum_{j \in E_{\bar{n}}} |\bar{x}_{j+e_i}|^2 \end{aligned}$$

with periodic boundary conditions  $\bar{x}_{j+\bar{n}e_i} = \bar{x}_j$ , where

$$j = (j_1, j_2, j_3), \quad e_1 = (1, 0, 0), e_2 = (0, 1, 0), e_3 = (0, 0, 1),$$

$\bar{n}^3 = n$  and  $c$  is a positive constant independent of  $n$ . The sequence  $\{\eta_n\}_n \subset (0, \infty)$  is introduced to make the potential strictly convex for any fixed  $n$ , while we also assume that for some  $0 < \delta_1 < \delta_2 < 1/2$  and constants  $c_2 > c_1 > 0$

$$(19) \quad c_1 n^{-1/2+\delta_1} \leq \eta_n \leq c_2 n^{-1/2+\delta_2}.$$

We will see in (32) that the upper bound in (19) is needed in our model to obtain non zero friction matrices  $\kappa$ , and by (14), the lower bound in (19) implies that  $\|\partial_{X^\ell} a\|_{\ell^\infty}$  remains bounded, provided  $\|\beta_{\ell,\cdot}\|_{\ell^1}$  is bounded. We note that  $\bar{V}''$  consists of the standard finite difference matrix with mesh size one related to the Laplacian in  $\mathbb{R}^3$  and a small positive definite perturbation  $\eta_n^2 \mathbf{I}$ , where  $\mathbf{I}$  is the corresponding identity matrix. The minimum of the potential is obtained for the position deviations  $\bar{x}_j = 0$ ,  $j \in E_{\bar{n}}$ , which we may view as the  $n$  heat bath particles located on the  $n$  different lattice points in  $E_{\bar{n}}$ . This heat bath model can be extended to positions  $\bar{x}_j \in \mathbb{R}^3$ , see Remark 1, and we note that the first double sum in (18) forms a matrix which for each row has a positive diagonal element which is equal to the negative sum of all off diagonal elements elements as for  $\bar{V}''$  in (17).

In each coordinate direction the discrete Laplacian is a circulant matrix so that the eigenvectors and eigenvalues can be written

$$(20) \quad \begin{aligned} \nu_k(j) &= e^{2\pi i j \cdot k / \bar{n}}, \quad j_i = -\bar{n}/2, \dots, \bar{n}/2 - 1, \quad \text{and} \quad k_i = -\bar{n}/2, \dots, \bar{n}/2 - 1, \\ \omega_k^2 &= c^2 \sum_{i=1}^3 2(1 - \cos(\frac{2\pi k_i}{\bar{n}})) + \eta_n^2, \end{aligned}$$

and  $\|\nu_k\|_2^2 = \sum_{i=1}^3 \sum_{j_i=-\bar{n}/2}^{\bar{n}/2-1} |\nu_k(j)|^2 = \bar{n}^3$ . Let  $\mathbf{r} := (\frac{k_1}{\bar{n}}, \frac{k_2}{\bar{n}}, \frac{k_3}{\bar{n}})$  and  $r := |\mathbf{r}|$ . We have for  $k = \bar{n}\mathbf{r}$  by (19)

$$\begin{aligned} \nu_k(j) &= e^{2\pi i j \cdot \mathbf{r}} =: \nu(\mathbf{r}, j), \\ \lim_{n \rightarrow \infty} \omega_k^2 &= c^2 \sum_{i=1}^3 2(1 - \cos(2\pi r_i)) =: (\omega(\mathbf{r}))^2, \end{aligned}$$

and we have assumed in (13) that the derivative of the force has a limit

$$(21) \quad \lim_{n \rightarrow \infty} F'_{\ell,j} = \bar{F}_{\ell,j},$$

which implies

$$(22) \quad \begin{aligned} \lim_{\substack{n \rightarrow \infty \\ \frac{k}{\bar{n}} = \mathbf{r}}} \beta_{\ell,k} &= \sum_{j \in E_\infty} \bar{F}_{\ell,j} \nu^*(\mathbf{r}, j) =: \beta_\ell(\mathbf{r}), \\ \beta_\ell(0) &= \sum_{j \in E_\infty} \bar{F}_{\ell,j}, \end{aligned}$$

that is, the function  $\beta_\ell : [-1/2, 1/2]^3 \rightarrow \mathbb{R}$  has the Fourier coefficients  $\bar{F}_{\ell,j}$ . The value  $\beta_\ell(0)$  will be used in (32) to determine the friction matrix  $\kappa$ .

**Remark 1.** The heat bath model (18) can be extended to have  $\bar{x}_j = x_j - a_j(X) \in \mathbb{R}^3$ , with  $\bar{x}_j = (\bar{x}_j^1, \bar{x}_j^2, \bar{x}_j^3)$ . In the case

$$\langle \bar{V}'' \bar{x}, \bar{x} \rangle = \sum_{k=1}^3 \sum_{i=1}^3 \sum_{j \in E_{\bar{n}}} c_k^2 (-\bar{x}_{j+e_i}^k + 2\bar{x}_j^k - \bar{x}_{j-e_i}^k) \bar{x}_j^k + \eta_n^2 \sum_{i=1}^3 \sum_{j \in E_{\bar{n}}} |\bar{x}_{j+e_i}|^2$$

we still have the same eigenvalues if  $c_k^2 = c^2$ , so the model does not change in principle. If on the other hand the constants  $c_k$  are different for the different components of  $\bar{x}_j$  the spectrum may change and we obtain a different heat bath model.

3.1.3. *The limit friction matrix.* We can take the limit as  $\bar{n} \rightarrow \infty$  in (15), while  $\mathbf{r} = k/\bar{n}$  is constant, to obtain an integral

$$\begin{aligned}
(23) \quad \lim_{n \rightarrow \infty} K_n^{\ell \ell'}(\tau) &= \lim_{n \rightarrow \infty} \sum_k \cos(\tau \omega_k) \frac{\beta_{\ell, k}^* \beta_{\ell', k}}{\omega_k^2 \|\nu_k\|_2^2} \\
&= \int_{[-\frac{1}{2}, \frac{1}{2}]^3} \cos(\tau \omega(\mathbf{r})) \frac{\beta_{\ell}^*(\mathbf{r}) \beta_{\ell'}(\mathbf{r})}{(\omega(\mathbf{r}))^2} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\
&=: K_{\infty}^{\ell \ell'}(\tau).
\end{aligned}$$

The change of variables  $\omega_i = 2^{1/2} c \sqrt{1 - \cos(2\pi r_i)} \operatorname{sgn}(r_i)$  yields, with the spherical coordinate  $\omega = (\cos \alpha \cos \theta, \sin \alpha \cos \theta, \sin \theta) \omega$ ,

$$\begin{aligned}
(24) \quad &\lim_{n \rightarrow \infty} \sum_k \cos(\tau \omega_k) \frac{\beta_{\ell, k}^* \beta_{\ell', k}}{\omega_k^2 \|\nu_k\|_2^2} \\
&= \int_{\omega \in [-\frac{1}{2}, \frac{1}{2}]^3} \cos(\tau \omega) \beta_{\ell}^*(\mathbf{r}(\omega)) \beta_{\ell'}(\mathbf{r}(\omega)) \prod_{i=1}^3 \left( \frac{\sqrt{1 - \cos(2\pi r_i(\omega_i))}}{2^{1/2} \pi c \sin(2\pi r_i(\omega_i))} \right) \frac{d\omega}{|\omega|^2} \\
&= \int_{\omega \in [-\frac{1}{2}, \frac{1}{2}]^3} \cos(\tau \omega) f(\omega, \ell, \ell') \frac{d\omega}{|\omega|^2} \\
&= \int_0^{\pi} \int_0^{2\pi} \int_0^{\infty} \cos(\tau \omega) f(\omega, \ell, \ell') \sin \theta d\omega d\alpha d\theta
\end{aligned}$$

where

$$(25) \quad f(\omega, \ell, \ell') := \begin{cases} \beta_{\ell'}(\omega) \beta_{\ell}^*(\omega) \prod_{i=1}^3 \pi^{-1} (4c^2 - \omega_i^2)^{-1/2}, & -2c < \omega_i < 2c, \\ 0, & \text{otherwise.} \end{cases}$$

with  $\beta(\omega) := \beta(r(\omega))$ . The term  $(4c^2 - \omega_i^2)^{-1/2}$  is unbounded (but integrable) at the boundary where  $\omega_i = \pm 2c$ . For the purpose of simplifying later proofs we will assume that  $\beta_{\ell}(\omega)$  is two times differentiable and that it vanishes at the boundary of  $\omega \in [-\frac{1}{2}, \frac{1}{2}]^3 = [-2c, 2c]^3$  as follows:

$$(26) \quad \beta(\omega) = 0 \text{ for } \omega \in [-2c, 2c]^3 \text{ satisfying } \omega = |\omega| > c.$$

**Remark 2** (Density of states relates to  $c$ ). We also note that the Jacobian determinant in (24)

$$(27) \quad \left| \frac{d\mathbf{r}(\omega)}{d\omega} \right| = \prod_{i=1}^3 \frac{dr_i}{d\omega_i} = \prod_{i=1}^3 \pi^{-1} (4c^2 - \omega_i^2)^{-1/2}$$

is related to the density

$$|\nabla \omega(\mathbf{r})|^{-1} = \pi^{-1} (12c^2 - \omega^2)^{-1/2}$$

of the density of states

$$\int_{[-1/2, 1/2]^3} \delta(\bar{\omega} - \omega(\mathbf{r})) d\mathbf{r} = \int_{\omega(\mathbf{r}) = \bar{\omega}} \frac{dS}{|\nabla \omega(\mathbf{r})|}$$

evaluated by the co-area formula, where  $dS$  is the Lebesgue surface measure on the surface  $\{\mathbf{r} : \omega(\mathbf{r}) = \bar{\omega}\}$  for a given frequency  $\bar{\omega} \in [0, \infty)$ .

We are now ready to formulate the limit as  $n \rightarrow \infty$  in the friction term based on the constant  $N \times N$  friction matrix  $\kappa$ .

**Lemma 3.1.** *Let*

$$\kappa_{\ell\ell'} := \frac{1}{4\pi c^3} \left( \sum_{j \in E_\infty} \bar{F}_{\ell j} \right) \left( \sum_{j \in E_\infty} \bar{F}_{\ell' j} \right)$$

and assume that (3),(4), (7), (11), (13), (18), (26) hold and for each  $t > 0$  and  $(X_0, P_0)$  there is a constant  $C$  such that

$$\sup_{0 \leq s \leq t} (\mathbb{E}[|\dot{P}_s|^2])^{1/2} + \sup_{0 \leq s \leq t} (\mathbb{E}[|\dot{X}_s|^2])^{1/2} \leq C,$$

then for any function  $h \in L^\infty(\mathbb{R}^{2N})$

$$(28) \quad \lim_{n \rightarrow \infty} \mathbb{E}[h(X_t, P_t) \int_0^t \langle \bar{V}'' \cos\left(\frac{(t-s)\sqrt{\bar{V}''}}{\sqrt{m}}\right) \dot{a}(X_s), \partial_{X^\ell} a \rangle ds] \\ = \mathbb{E}[m^{1/2} h(X_t, P_t) \kappa \dot{X}_t] + \mathcal{O}(m \log m^{-1}).$$

**Remark 3** (Dirchlet boundary condition). If we replace the periodic boundary conditions in the heat bath model (20) with homogenous Dirichlet conditions, we have instead

$$\nu_k(j) = \prod_{i=1}^3 \sin\left(\frac{\pi k_i}{2} + \frac{\pi j_i k_i}{\bar{n} + 1}\right), \quad j_i = -\bar{n}/2, \dots, \bar{n}/2 - 1, \quad \text{and } k_i = 1, \dots, \bar{n}, \\ \omega_k^2 = c^2 \sum_{i=1}^3 2\left(1 - \cos\left(\frac{\pi k_i}{\bar{n} + 1}\right)\right) + \eta_n^2, \\ \lim_{\bar{n} \rightarrow \infty} \frac{\bar{n}^3}{\|\nu_k\|_2^2} = 8.$$

We can write the eigenvectors as functions of  $k_i/(\bar{n} + 1)$  since

$$\sin\left(\frac{\pi k_i}{2} + \frac{\pi j_i k_i}{\bar{n} + 1}\right) = \begin{cases} \sin\left(\frac{\pi j_i k_i}{\bar{n} + 1}\right) & \text{if } \text{mod}(k_i, 4) = 0, \\ \cos\left(\frac{\pi j_i k_i}{\bar{n} + 1}\right) & \text{if } \text{mod}(k_i, 4) = 1, \\ -\sin\left(\frac{\pi j_i k_i}{\bar{n} + 1}\right) & \text{if } \text{mod}(k_i, 4) = 2, \\ -\cos\left(\frac{\pi j_i k_i}{\bar{n} + 1}\right) & \text{if } \text{mod}(k_i, 4) = 3, \end{cases}$$

and split the sum over  $k_i$  into one sum over odd  $k_i$ , where the eigenvector is based on cosine functions, and one sum over even  $k_i$ , where the eigenvector is based on sine functions. With these changes, the derivation of  $\kappa$  follows as in the case with periodic boundary conditions.

*Proof of Lemma 3.1.* To study the decay as  $\tau \rightarrow \infty$  of the kernel  $K_\infty$ , we use (26) and the shorthand  $f(\boldsymbol{\omega}) := f(\boldsymbol{\omega}, \cdot, \cdot)$  and integrate by parts

$$\begin{aligned}
K_\infty(\tau) &= \int_{\mathbb{R}^3} \cos(\tau\boldsymbol{\omega}) f(\boldsymbol{\omega}) \frac{d\boldsymbol{\omega}}{\omega^2} \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty \cos(\tau\boldsymbol{\omega}) f(\boldsymbol{\omega}) \sin\theta d\omega d\alpha d\theta \\
&= - \int_0^\pi \int_0^{2\pi} \int_0^\infty \frac{\sin(\tau\boldsymbol{\omega})}{\tau} \partial_\omega f(\boldsymbol{\omega}) \sin\theta d\omega d\alpha d\theta \\
&= - \int_0^\pi \int_0^{2\pi} \frac{1}{\tau^2} \partial_\omega f(\boldsymbol{\omega})|_{\omega=0} \sin\theta d\alpha d\theta \\
&\quad - \int_0^\pi \int_0^{2\pi} \int_0^\infty \frac{\cos(\tau\boldsymbol{\omega})}{\tau^2} \partial_\omega^2 f(\boldsymbol{\omega}) \sin\theta d\omega d\alpha d\theta.
\end{aligned}$$

Since  $f(\boldsymbol{\omega})$  has its support in  $\omega = |\boldsymbol{\omega}| \leq c$ , cf. (26), and the second derivative  $\partial_\omega^2 f(\boldsymbol{\omega})$  is bounded, we obtain

$$(29) \quad \|K_\infty(\tau)\| = \left\| \int_{\mathbb{R}^3} \cos(\tau\boldsymbol{\omega}) f(\boldsymbol{\omega}) \frac{d\boldsymbol{\omega}}{\omega^2} \right\| = \mathcal{O}((1 + \tau)^{-2}).$$

For a given  $t > 0$  and bounded function  $h : \mathbb{R}^N \times \mathbb{R}^N \rightarrow \mathbb{R}$  we next study the expectation of

$$\begin{aligned}
&\lim_{n \rightarrow \infty} h(X_t, P_t) \int_0^t \langle \bar{V}'' \cos\left(\frac{(t-s)\sqrt{\bar{V}''}}{\sqrt{m}}\right) \dot{a}(X_s), \partial_{X^\ell} a \rangle ds \\
&= \sqrt{m} \lim_{n \rightarrow \infty} h(X_t, P_t) \int_0^{t/\sqrt{m}} \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \dot{a}(X_{t-\sqrt{m}\tau}), \partial_{X^\ell} a \rangle d\tau.
\end{aligned}$$

Let  $\tau_* = m^{-1/2} \min(t, 1)$  and split the integral

$$\begin{aligned}
&h(X_t, P_t) \int_0^{t/\sqrt{m}} \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \dot{a}(X_{t-\sqrt{m}\tau}), \partial_{X^\ell} a \rangle d\tau \\
(30) \quad &= h(X_t, P_t) \int_0^{\tau_*} \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \dot{a}(X_{t-\sqrt{m}\tau}), \partial_{X^\ell} a \rangle d\tau \\
&\quad + h(X_t, P_t) \int_{\tau_*}^{t/\sqrt{m}} \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \dot{a}(X_{t-\sqrt{m}\tau}), \partial_{X^\ell} a \rangle d\tau.
\end{aligned}$$

The magnitude of the second integral is zero if  $t \leq 1$ , and otherwise  $\tau_* = m^{-1/2} < tm^{-1/2}$  and the integral is bounded in expectation using (15), (23) and (29):

$$\begin{aligned}
&\mathbb{E} \left[ \left| h(X_t, P_t) \int_{1/\sqrt{m}}^{t/\sqrt{m}} \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \dot{a}(X_{t-\sqrt{m}\tau}), \partial_{X^\ell} a \rangle d\tau \right| \right] \\
&\leq \int_{1/\sqrt{m}}^{t/\sqrt{m}} \frac{C \mathbb{E}[|h(X_t, P_t)| |\dot{X}_{t-m^{1/2}\tau}|]}{\tau^2} d\tau \\
&\leq C \sup_{0 \leq s \leq t} (\mathbb{E}[|\dot{X}_s|^2])^{1/2} (\mathbb{E}[|h(X_t, P_t)|^2])^{1/2} \sqrt{m}.
\end{aligned}$$

The expectation and the limit  $n \rightarrow \infty$  of the first integral in the right hand side of (30) can be written as

$$\begin{aligned} & \mathbb{E}[h(X_t, P_t) \int_0^{\tau_*} \int_0^\pi \int_0^{2\pi} \int_0^\infty \cos(\tau\omega) f(\boldsymbol{\omega}) \sin \theta d\omega d\alpha d\theta \dot{X}_t d\tau] \\ & - \mathbb{E}[h(X_t, P_t) \int_0^{\tau_*} \int_0^\pi \int_0^{2\pi} \int_0^\infty \cos(\tau\omega) f(\boldsymbol{\omega}) \sin \theta d\omega d\alpha d\theta (\dot{X}_t - \dot{X}_{t-\tau\sqrt{m}}) d\tau], \end{aligned}$$

where, using (29),

$$\begin{aligned} & \left| \mathbb{E} \left[ h(X_t, P_t) \int_0^{\tau_*} \int_0^\pi \int_0^{2\pi} \int_0^\infty \cos(\tau\omega) f(\boldsymbol{\omega}) \sin \theta d\omega d\alpha d\theta (\dot{X}_t - \dot{X}_{t-\tau\sqrt{m}}) d\tau \right] \right| \\ & \leq \mathbb{E} \left[ \left| h(X_t, P_t) \int_0^{\tau_*} \int_0^\pi \int_0^{2\pi} \int_0^\infty \cos(\tau\omega) f(\boldsymbol{\omega}) \sin \theta d\omega d\alpha d\theta \int_{-\tau\sqrt{m}}^0 \ddot{X}_{t+s} ds d\tau \right|^2 \right]^{1/2} \\ & \leq C\sqrt{m} \int_0^{\tau_*} \frac{\tau}{1+\tau^2} d\tau \sup_{0 \leq s \leq t} (\mathbb{E}[|\ddot{X}_s|^2])^{1/2} (\mathbb{E}[|h(X_t, P_t)|^2])^{1/2} \\ & \leq C\sqrt{m} \min(1, \log m^{-1}) \sup_{0 \leq s \leq t} (\mathbb{E}[|\dot{X}_s|^2])^{1/2} (\mathbb{E}[|h(X_t, P_t)|^2])^{1/2}. \end{aligned}$$

We prove in Section 3.3 that the expected value  $\sup_{0 \leq s \leq t} (\mathbb{E}[|\dot{X}_s|^2 + |\ddot{X}_s|^2])$  is bounded, and these properties imply that  $\mathbb{E}[|h(X_t, P_t)|^2]$  also is bounded. Consequently,

(31)

$$\begin{aligned} & \lim_{n \rightarrow \infty} \mathbb{E}[h(X_t, P_t) \int_0^t \langle \bar{V}'' \cos(\frac{(t-s)\sqrt{\bar{V}''}}{\sqrt{m}}) \dot{a}(X_s), \partial_{X^\ell} a \rangle ds] \\ & - \mathbb{E}[m^{1/2} h(X_t, P_t) \sum_{\ell'} \int_0^{\tau_*} \int_0^\pi \int_0^{2\pi} \int_0^\infty \cos(\tau\omega) f(\boldsymbol{\omega}, \ell, \ell') \sin \theta d\omega d\alpha d\theta d\tau \dot{X}_t^{\ell'}] \\ & = \mathcal{O}(m \log m^{-1}). \end{aligned}$$

The Fourier transform of  $f(\boldsymbol{\omega})$  with respect to  $\omega$  is integrable and since  $f(\boldsymbol{\omega})$  is continuous, the Fourier inversion property and (22) yield that

$$\begin{aligned} & \lim_{m \rightarrow 0^+} \sum_{\ell'} \int_0^{\tau_*} \int_0^\infty \int_0^{2\pi} \int_0^\pi \cos(\tau\omega) f(\boldsymbol{\omega}, \ell, \ell') \sin \theta d\theta d\alpha d\omega d\tau \dot{X}_t^{\ell'} \\ & = \sum_{\ell'} \int_0^\infty \int_0^\infty \int_0^{2\pi} \int_0^\pi \cos(\tau\omega) f(\boldsymbol{\omega}, \ell, \ell') \sin \theta d\theta d\alpha d\omega d\tau \dot{X}_t^{\ell'} \\ & = \frac{\pi}{2} \sum_{\ell'} \lim_{\omega \rightarrow 0} \int_0^{2\pi} \int_0^\pi f(\boldsymbol{\omega}, \ell, \ell') \sin \theta d\theta d\alpha \dot{X}_t^{\ell'} \\ & = 2\pi^2 \sum_{\ell'} f(0, \ell, \ell') \dot{X}_t^{\ell'} \\ & = \frac{1}{4\pi c^3} \sum_{\ell'} \left( \sum_{j \in E_\infty} \bar{F}_{\ell j} \right) \left( \sum_{j \in E_\infty} \bar{F}_{\ell' j} \right) \dot{X}_t^{\ell'} \\ & = \sum_{\ell'} \kappa_{\ell \ell'} \dot{X}_t^{\ell'}. \end{aligned} \tag{32}$$

That is, the friction matrix,

$$\kappa_{\ell\ell'} := \frac{1}{4\pi c^3} \left( \sum_{j \in E_\infty} \bar{F}_{\ell j} \right) \left( \sum_{j \in E_\infty} \bar{F}_{\ell' j} \right)$$

in the Langevin equation is determined by the  $\partial_{X^\ell}$ -derivative of the sum of forces on all bath particles. Equation (28) follows from (31) and (32).  $\square$

**Remark 4** (Vanishing friction). If the heat bath model is modified to have nearest neighbor interactions in a lattice in dimension  $d$ , we obtain as in (32)

$$\kappa_{\ell\ell'} = S_d \lim_{\omega \rightarrow 0} f(\boldsymbol{\omega}, \ell, \ell') \omega^{d-1} / \omega^2 = S_d \lim_{\omega \rightarrow 0} \beta_\ell(\boldsymbol{\omega}) \beta_{\ell'}^*(\boldsymbol{\omega}) \omega^{d-3}$$

where  $S_d$  is a positive constant related to the dimension  $d$ . We see that under the assumption  $\beta_\ell(0^+) \beta_{\ell'}(0^+) > 0$ , it is only in dimension  $d = 3$  that this heat bath generates a positive definite friction matrix  $\kappa$ . For  $d < 3$  we obtain  $\kappa = \infty$  and for  $d > 3$  we have  $\kappa = 0$ .

If we change the heat bath potential energy to be based on any circulant matrix in each dimension, we have the requirement

$$(33) \quad \lim_{\omega \rightarrow 0} \frac{r^2(\boldsymbol{\omega}) \frac{dr}{d\omega}}{\omega^2} = \text{constant}$$

to obtain a positive definite friction matrix  $\kappa$ , in dimension  $d = 3$ . This limit for the eigenvalues  $\omega^2$  implies that  $\bar{V}''$  becomes a difference quotient approximation of the Laplacian with mesh size one. We conclude that (33) leads to a choice of  $\bar{V}''$  in (18) that is another discretization of the Laplacian or discretizations that tends to the Laplacian as  $n \rightarrow \infty$ .

**3.2. The fluctuation term.** The initial distribution of  $\varphi_0 = \sum_k (\gamma_k^r + i\gamma_k^i) \nu'_k$ , determined by the Gibbs distribution of the Hamiltonian system in (7) and (9), shows that all  $\gamma_k^r$  and  $\gamma_k^i$  are independent and normal distributed with mean zero and variance  $T/\omega_k^2$ . This initial data provides the fluctuation term in (10), namely

$$(34) \quad \begin{aligned} \zeta_t^\ell &= \text{Re} \langle e^{-it\sqrt{\bar{V}''}/\sqrt{m}} \varphi_0, \bar{V}'' \partial_{X^\ell} a \rangle \\ &= \sum_k \text{Re} \left( e^{it\omega_k/\sqrt{m}} \frac{\gamma_k^*}{n^{3/2}} \langle \nu_k, \bar{V}'' \partial_{X^\ell} a \rangle \right) \\ &= \sum_k \text{Re} \left( e^{it\omega_k/\sqrt{m}} \frac{\gamma_k^*}{n^{1/2}} \beta_{k,\ell} \right), \end{aligned}$$

which has the special property that its covariance satisfies

$$(35) \quad \begin{aligned} \mathbb{E}[\zeta_t^\ell \zeta_s^{\ell'}] &= \mathbb{E}[\text{Re} \langle e^{-it\sqrt{\bar{V}''}/\sqrt{m}} \varphi_0, \bar{V}'' \partial_{X^\ell} a \rangle \text{Re} \langle e^{-is\sqrt{\bar{V}''}/\sqrt{m}} \varphi_0, \bar{V}'' \partial_{X^{\ell'}} a \rangle] \\ &= T \langle \cos((t-s)\sqrt{\bar{V}''}/\sqrt{m}) \bar{V}'' \partial_{X^\ell} a, \partial_{X^{\ell'}} a \rangle \end{aligned}$$

that is, the covariance is  $T$  times the friction integral kernel, as observed in [28]. We repeat a proof for our setting here, where we also show that the limit of  $\zeta_t$  as  $n \rightarrow \infty$  is well defined.

*Proof of (35).* Let  $e^{-it\sqrt{\bar{V}''}/\sqrt{m}} =: S_{t0}$  and write  $e^{-it\sqrt{\bar{V}''}/\sqrt{m}} \varphi_0 = S_{ts} S_{s0} \varphi_0$ . Since the operator  $S_{s0}$  is unitary, we have  $S_{s0} \varphi_0 = \sum_k \gamma'_k \nu'_k$  where  $\{\nu'_k\}$  is the set of normalized real valued eigenvectors of  $\bar{V}''$ , defined in (7). The random coefficients



$\gamma'_k = \gamma'_{k,r} + i\gamma'_{k,i}$  are based on  $\gamma'_{k,r}$  and  $\gamma'_{k,i}$  which are independent normal distributed with mean zero and variance  $T/\omega_k^2$ , for  $k = (k_1, k_2, k_3)$  and  $k_i = 1, \dots, \bar{n}$ . Use the orthonormal real-valued basis  $\{\nu'_k\}$  to obtain

$$\begin{aligned}
 & \mathbb{E}[\zeta_t^\ell \zeta_s^{\ell'}] \\
 &= \mathbb{E}\left[\sum_{k,k'} \langle \text{Re}(S_{t0}(\gamma_k^r + i\gamma_k^i)\nu'_k), \bar{V}'' \partial_{X_\ell} a \rangle \langle \text{Re}(S_{s0}(\gamma_{k'}^r + i\gamma_{k'}^i)\nu'_{k'}), \bar{V}'' \partial_{X_{\ell'}} a \rangle\right] \\
 &= \mathbb{E}\left[\sum_{k,k'} \langle \text{Re}(S_{ts}(\gamma'_{k,r} + i\gamma'_{k,i})\nu'_k), \bar{V}'' \partial_{X_\ell} a \rangle \langle \text{Re}((\gamma'_{k',r} + i\gamma'_{k',i})\nu'_{k'}), \bar{V}'' \partial_{X_{\ell'}} a \rangle\right] \\
 &= \mathbb{E}\left[\sum_{k,k'} \langle \omega_k^2 \left( \cos((t-s)\omega_k m^{-1/2})\gamma'_{k,r} - \sin((t-s)\omega_k m^{-1/2})\gamma'_{k,i} \right) \nu'_k, \partial_{X_\ell} a \rangle \right. \\
 &\quad \left. \times \langle \gamma'_{k',r} \nu'_{k'}, \bar{V}'' \partial_{X_{\ell'}} a \rangle\right] \\
 &= \sum_{k,k'} \left( \langle \omega_k^2 \left( \cos((t-s)\omega_k m^{-1/2}) \mathbb{E}[\gamma'_{k,r} \gamma'_{k',r}] \right. \right. \\
 &\quad \left. \left. - \sin((t-s)\omega_k m^{-1/2}) \mathbb{E}[\gamma'_{k,i} \gamma'_{k',r}] \right) \nu'_k, \partial_{X_\ell} a \rangle \langle \nu'_{k'}, \bar{V}'' \partial_{X_{\ell'}} a \rangle \right) \\
 &= \sum_k T \langle \cos((t-s)\sqrt{\bar{V}''}/\sqrt{m}) \nu'_k, \partial_{X_\ell} a \rangle \langle \nu'_k, \bar{V}'' \partial_{X_{\ell'}} a \rangle \\
 &= T \langle \cos((t-s)\sqrt{\bar{V}''}/\sqrt{m}) \partial_{X_\ell} a, \bar{V}'' \partial_{X_{\ell'}} a \rangle.
 \end{aligned}$$

We conclude that  $\zeta$  is a Gaussian process with mean zero and covariance (35). The fluctuation-dissipation property (35), the limit (23) and the bound (29) show that the covariance matrix has a limit as  $n \rightarrow \infty$ :

$$(36) \quad \lim_{n \rightarrow \infty} \mathbb{E}[\zeta_t \zeta_s] = TK_\infty \left( \frac{t-s}{\sqrt{m}} \right).$$

Therefore  $\zeta$  has a well defined limit, in the  $L^2$ -space with norm  $(\int_0^\tau \mathbb{E}[|\zeta_t|^2] dt)^{1/2}$ , for any finite time  $\tau$  as  $n \rightarrow \infty$ .  $\square$

**3.3. The system dynamics.** We can write the system dynamics (6) and (10) as

$$\begin{aligned}
 (37) \quad & X_t = X_0 + \int_0^t P_s ds, \\
 & P_t = P_0 - \int_0^t \nabla \lambda(X_s) ds + \int_0^t \text{Re} \langle \varphi_s, \bar{V}'' \nabla a \rangle ds \\
 &= P_0 - \int_0^t \nabla \lambda(X_s) ds - \int_0^t \int_0^s \text{Re} \langle e^{-i(s-\sigma)\bar{V}'' m^{-1/2}} (P_\sigma \cdot \nabla) a, \bar{V}'' \nabla a \rangle d\sigma ds \\
 &\quad + \int_0^t \zeta_s ds.
 \end{aligned}$$

We assume that

$$(38) \quad \lambda \text{ is three times continuously differentiable and } \sup_X \|\text{D}^2 \lambda(X)\| + \sup_X \|\text{D}^3 \lambda(X)\| \text{ is bounded}$$

and apply Cauchy's inequality on (37) to obtain

$$(39) \quad \begin{aligned} \frac{d}{dt} \int_0^t |X_s|^2 + |P_s|^2 ds &= |X_t|^2 + |P_t|^2 \\ &\leq C \left( 1 + (t+t^3) \int_0^t (|X_s|^2 + |P_s|^2) ds + t \int_0^t |\zeta_s|^2 ds \right), \end{aligned}$$

which implies there is a constant  $C$ , depending on  $(X_0, P_0)$ , such that

$$\frac{d}{dt} \int_0^t \mathbb{E}[|X_s|^2 + |P_s|^2] ds \leq C \left( 1 + (t+t^3) \int_0^t \mathbb{E}[|X_s|^2 + |P_s|^2] ds + \underbrace{t \int_0^t \mathbb{E}[|\zeta_s|^2] ds}_{\leq t^2 T \text{trace}(K_\infty(0))} \right).$$

Here  $D^k \lambda$  denotes the set of all partial derivatives of order  $k$  and if  $k = 1$  or  $k = 2$  we identify it with the gradient and the Hessian, respectively. Integration yields the Gronwall inequality

$$\int_0^t \mathbb{E}[|X_s|^2 + |P_s|^2] ds \leq C e^{Ct^4},$$

which by (39) and the mean square of

$$\dot{P}_t = -\nabla \lambda(X_t) + \int_0^t \text{Re} \langle e^{-i(t-s)\bar{V}''} m^{-1/2} (P_s \cdot \nabla) a, \bar{V}'' \nabla a \rangle ds + \zeta_t$$

establishes

**Lemma 3.2.** *Suppose that the assumptions in Lemma 3.1 and (38) hold, then for each  $t > 0$  and  $(X_0, P_0)$  there is a constant  $C$  such that*

$$\sup_{0 \leq s \leq t} \mathbb{E}[|X_s|^2 + |P_s|^2 + |\dot{P}_s|^2] \leq C(1 + e^{Ct^4}).$$

**3.4. Approximation by Langevin dynamics.** In this section we approximate the Hamiltonian dynamics (6) by the Langevin dynamics (12)

$$\begin{aligned} dX_L(t) &= P_L(t) dt, \\ dP_L(t) &= -\nabla \lambda(X_L(t)) dt - m^{1/2} \kappa P_L(t) dt + (2m^{1/2} \kappa T)^{1/2} dW(t), \\ X_L(0) &= X(0), \\ P_L(0) &= P(0). \end{aligned}$$

To analyse the approximation we use that,

(40)

for any infinitely differentiable function  $g : \mathbb{R}^{2N} \rightarrow \mathbb{R}$  with compact support,

the expected value

$$u(z, s) = \mathbb{E}[g(X_L(t_*), P_L(t_*)) \mid (X_L(s), P_L(s)) = z], \quad s < t_* \text{ and } z \in \mathbb{R}^{2N},$$

is well defined, since the Langevin equation (12), for  $Z_t := (X_L(t), P_L(t))$ , has Lipschitz continuous drift and constant diffusion coefficient. The assumption (38) implies that the stochastic flows  $\frac{\partial Z_t}{\partial Z_s}$  and  $\frac{\partial^2 Z_t}{\partial Z_s^2}$  also are well defined, which implies that the function  $u$  has bounded and continuous derivatives up to order two in  $z$

and to order one in  $t$ , see [12] and [8], and solves the corresponding Kolmogorov equation

$$\begin{aligned} & \partial_s u(X, P, s) + P \cdot \nabla_X u(X, P, s) - (\nabla \lambda(X) + \sqrt{m} \kappa P) \cdot \nabla_P u(X, P, s) \\ & + \sum_{j,k=1}^N \sqrt{m} T \kappa_{jk} \partial_{P_j P_k} u(x, P, s) = 0, \quad s < t_*, \\ & u(X, P, t_*) = g(X, P). \end{aligned}$$

We have

$$\begin{aligned} (41) \quad & \mathbb{E}[g(X(t_*), P(t_*)) \mid X_0, P_0] - \mathbb{E}[g(X_L(t_*), P_L(t_*)) \mid (X_L(0), P_L(0)) = (X_0, P_0)] \\ & = \mathbb{E}[u(X(t_*), P(t_*), t_*) - u(X(0), P(0), 0) \mid X_0, P_0] \\ & = \int_0^{t_*} \mathbb{E}[du(X(t), P(t), t) \mid X_0, P_0] \\ & = \int_0^{t_*} \mathbb{E}[\partial_t u(X_t, P_t, t) + P_t \cdot \nabla_X u(X_t, P_t, t) + \dot{P}_t \cdot \nabla_P u(X_t, P_t, t) \mid X_0, P_0] dt \\ & = \int_0^{t_*} \mathbb{E}[(\dot{P}_t + \nabla \lambda(X_t) + \sqrt{m} \kappa P_t) \cdot \nabla_P u(X_t, P_t, t) \\ & \quad - \sqrt{m} T \kappa : D_{PP}^2 u(X_t, P_t, t) \mid X_0, P_0] dt \\ & = \int_0^{t_*} \mathbb{E}[(\operatorname{Re} \langle \varphi_t, \bar{V}'' \nabla a \rangle + \sqrt{m} \kappa P_t) \cdot \nabla_P u(X_t, P_t, t) \\ & \quad - \sqrt{m} T \kappa : D_{PP}^2 u(X_t, P_t, t) \mid X_0, P_0] dt, \end{aligned}$$

where  $\kappa : D_{PP}^2 u := \sum_{\ell, \ell'} \kappa_{\ell, \ell'} \partial_{P_\ell} \partial_{P_{\ell'}} u$ .

**Lemma 3.3.** *Suppose that the assumptions in Lemma 3.2 and (40) hold, then*

$$\begin{aligned} (42) \quad & \lim_{n \rightarrow \infty} \mathbb{E} \left[ \int_0^t \left\langle \cos \left( \frac{(t-s)\sqrt{V''}}{\sqrt{m}} \right) \dot{a}(X_s), \bar{V}'' \nabla a \cdot \nabla_P u(X_t, P_t) \right\rangle ds \mid X_0, P_0 \right] \\ & = m^{1/2} \mathbb{E}[\kappa \dot{X}_t \cdot \nabla_P u(X_t, P_t) \mid X_0, P_0] + \mathcal{O}(m \log m^{-1}). \end{aligned}$$

and

$$\begin{aligned} (43) \quad & \lim_{n \rightarrow \infty} \mathbb{E}[\langle \operatorname{Re}(e^{-itV''^{1/2}/\sqrt{m}} \varphi_0), \bar{V}'' \nabla a \cdot \nabla_P u(X_t, P_t, t) \rangle \mid X_0, P_0] \\ & = m^{1/2} T \mathbb{E}[\kappa : D_{PP} u(X_t, P_t, t) \mid X_0, P_0] + \mathcal{O}(m \log m^{-1}). \end{aligned}$$

The limit (42) is verified in (31) and we prove (43) below. The lemma and the error estimates (31) and (31) inserted in (41) imply

**Theorem 3.4.** *Provided the assumptions in Lemma 3.3 hold, then the Langevin dynamics (12) approximates the Hamiltonian dynamics (6) and (10), with the error estimate*

$$\begin{aligned} & \left| \mathbb{E}[g(X_{t_*}, P_{t_*}) \mid X_0, P_0] - \mathbb{E}[g(X_L(t_*), P_L(t_*)) \mid (X_L(0), P_L(0)) = (X_0, P_0)] \right| \\ & = \mathcal{O}(m \log \frac{1}{m}), \end{aligned}$$

where the rank one friction matrix is determined by the force  $\bar{F}$  from (14) and (21)

$$(44) \quad \begin{aligned} \kappa_{\ell\ell'} &= \frac{1}{4\pi c^3} \left( \sum_{j \in E_\infty} \bar{F}_{\ell j} \right) \left( \sum_{j' \in E_\infty} \bar{F}_{\ell' j'} \right) \\ &= \frac{1}{4\pi c^3} \sum_{(j, j') \in E_\infty} (\bar{V}'' \partial_{X^\ell} a(X))_j \sum_{j' \in E_\infty} (\bar{V}'' \partial_{X^{\ell'}} a(X))_{j'}. \end{aligned}$$

We see also that the alternative dynamics, with any friction coefficient  $\bar{\kappa} \geq 0$ ,

$$\begin{aligned} d\bar{X}_t &= \bar{P}_t dt \\ d\bar{P}_t &= -\nabla \lambda(\bar{X}_t) dt - \bar{\kappa} \bar{P}_t dt + (2\bar{\kappa} T)^{1/2} dW_t \end{aligned}$$

approximates (6) and (10) with the larger error

$$(45) \quad |\mathbb{E}[g(X_{t_*}, P_{t_*}) | X_0, P_0] - \mathbb{E}[g(\bar{X}_{t_*}, \bar{P}_{t_*}) | \bar{X}_0 = X_0, \bar{P}_0 = P_0]| = \mathcal{O}(\max(m^{1/2}, \|\bar{\kappa}\|)),$$

unless  $\bar{\kappa} = m^{1/2}\kappa$ .

*Proof of (43).* We have

$$(46) \quad \begin{aligned} \operatorname{Re}\langle \varphi_t, \bar{V}'' \nabla a \rangle &= \langle \operatorname{Re}(\underbrace{e^{-it\bar{V}''/m^{1/2}} \varphi_0}_{=: \varphi_1(t)}), \bar{V}'' \nabla a \rangle \\ &\quad - \int_0^t \langle \cos\left(\frac{t-s}{\sqrt{m}} \bar{V}''^{1/2}\right) \dot{a}(X_s), \bar{V}'' \nabla a \rangle ds \end{aligned}$$

and (42) shows that the second term cancels  $\sqrt{m}\kappa P_t \cdot \nabla_P u(X_t, P_t, t)$  to leading order in (41). It remains to show that the scalar product of  $\nabla_P u(X_t, P_t, t)$  and the first term in the right hand side (46) cancels the last term in (41).

To analyze the dependence between  $\partial_P u(X_t, P_t, t)$  and  $\operatorname{Re}\langle e^{-it\bar{V}''/m^{1/2}} \varphi_0, \bar{V}'' \nabla a \rangle$  from the initial data  $\varphi_0$  we will study how a small perturbation of  $\varphi_0$  influences  $\partial_P u(X_t, P_t, t)$ .

The proof has three steps:

- (1) to derive a representation of  $Z_t = (X_t, P_t)$  in terms of perturbations of the initial data  $\varphi_0 = \sum_k \gamma_k \nu'_k$  by removing one term,
- (2) to determine expected values  $\mathbb{E}[\langle e^{-it\bar{V}''^{1/2} m^{-1/2}} \varphi_0, h(Z_t) \rangle]$ , for a given function  $h$ , using Step (1), and
- (3) to evaluate (43), using the conclusion from Step (2) and the covariance result (35).

*Step 1. Claim.* Consider two different functions:  $\varphi_1(t)$  and  $\varphi_2(t) = \varphi_1(t) + \epsilon v(t)$ , where  $\epsilon \ll 1$ , then the corresponding solution paths  $Z_1 = (X_1, P_1)$  and  $Z_2 = (X_2, P_2)$  of the dynamics (6) (which can be written as (10)) based on the functions

$\varphi_1$  and  $\varphi_2$ , respectively, satisfy

$$\begin{aligned}
 (47) \quad Z_2(t) &= Z_1(t) + \sum_{\ell=1}^N \begin{bmatrix} \int_0^t G_{X_1 P_\ell}(t, s) \operatorname{Re}\langle \epsilon v(s), \bar{V}'' \partial_{X_\ell} a \rangle ds \\ \vdots \\ \int_0^t G_{X_N P_\ell}(t, s) \operatorname{Re}\langle \epsilon v(s), \bar{V}'' \partial_{X_\ell} a \rangle ds \\ \int_0^t G_{P_1 P_\ell}(t, s) \operatorname{Re}\langle \epsilon v(s), \bar{V}'' \partial_{X_\ell} a \rangle ds \\ \vdots \\ \int_0^t G_{P_N P_\ell}(t, s) \operatorname{Re}\langle \epsilon v(s), \bar{V}'' \partial_{X_\ell} a \rangle ds \end{bmatrix} \\
 &= Z_1(t) + \sum_{\ell=1}^N \int_0^t G_{\cdot P_\ell}(t, s) \operatorname{Re}\langle \epsilon v(s), \bar{V}'' \partial_{X_\ell} a \rangle ds
 \end{aligned}$$

where

$$G(t, s) = \begin{bmatrix} G_{XX}(t, s) & G_{XP}(t, s) \\ G_{PX}(t, s) & G_{PP}(t, s) \end{bmatrix} \in \mathbb{R}^{2N \times 2N}$$

solves the linear equation

$$\begin{aligned}
 (48) \quad \partial_t G_{Xy}(t, s) &= G_{Py}(t, s), \\
 \partial_t G_{Py}(t, s) &= - \int_0^1 D^2 \lambda(\tau X_1(t) + (1-\tau)X_2(t)) d\tau G_{Xy}(t, s) \\
 &\quad - \int_s^t \langle \bar{V}'' \cos\left(\frac{(t-r)\bar{V}''^{1/2}}{m^{1/2}}\right) \nabla a \cdot G_{Py}(r, s), \nabla a \rangle dr, \quad t > s, \quad y = X, P, \\
 G(s, s) &= \begin{bmatrix} \mathbf{I} & 0 \\ 0 & \mathbf{I} \end{bmatrix}.
 \end{aligned}$$

*Proof of the claim.* The linearized problem corresponding to (10) becomes

$$\begin{aligned}
 (49) \quad \frac{d}{dt} \bar{X}_t &= \bar{P}_t, \\
 \frac{d}{dt} \bar{P}_t &= - \int_0^1 D^2 \lambda(\tau X_1(t) + (1-\tau)X_2(t)) d\tau \bar{X}_t \\
 &\quad - \int_0^t \langle \bar{V}'' \cos\left(\frac{(t-s)\bar{V}''^{1/2}}{m^{1/2}}\right) \nabla a \cdot \bar{P}_s, \nabla a \rangle ds \\
 &\quad + \operatorname{Re}\langle e^{-it\bar{V}''/m^{1/2}} \bar{\varphi}_0, \bar{V}'' \nabla a \rangle, \quad t > 0.
 \end{aligned}$$

Consider  $R(t) := \operatorname{Re}\langle e^{-it\bar{V}''/m^{1/2}} \bar{\varphi}_0, \bar{V}'' \nabla a \rangle = \langle \epsilon v(t), \bar{V}'' \nabla a \rangle$  as a perturbation to the linearized equation (49) with  $\bar{Z}(t) := (\bar{X}_t, \bar{P}_t) = Z_2(t) - Z_1(t)$  and  $\bar{R}(t) := (0, R(t)) \in \mathbb{R}^{2N}$  and write (47) as

$$(50) \quad \bar{Z}(t) = \int_0^t G(t, s) \bar{R}(s) ds$$

and (48) in abstract form as

$$\begin{aligned}
 (51) \quad \partial_t G(t, s) &= A(t)G(t, s) - \int_s^t L(t, v)G(v, s)dv, \quad t > s, \\
 G(s, s) &= \mathbf{I}.
 \end{aligned}$$

Differentiation and change of the order of integration imply by (50) and (51)

$$\begin{aligned}
\frac{d}{dt}\bar{Z}(t) &= G(t, t)\bar{R}(t) + \int_0^t \partial_t G(t, s)\bar{R}(s)ds \\
&= \bar{R}(t) + A(t) \int_0^t G(t, s)\bar{R}(s)ds - \int_0^t \int_s^t L(t, v)G(v, s)\bar{R}(s)dvds \\
&= \bar{R}(t) + A(t)\bar{Z}_t - \int_0^t L(t, v) \int_0^v G(v, s)\bar{R}(s)dsdv \\
&= \bar{R}(t) + A(t)\bar{Z}(t) - \int_0^t L(t, v)\bar{Z}(v)dv,
\end{aligned}$$

which shows that (47) satisfies the linearized equation (49), and the claim is proved.

The main reason we use assumption (11), namely that  $\nabla a(X)$  is constant, is to obtain this linearized equation for  $G$ , which otherwise would include the term  $\text{Re}\langle \varphi, \bar{V}''D^2a \rangle$  that would introduce the fast time scale of  $\varphi$  in  $G$ , which we now avoid.

*Step 2.* We will use

$$\varphi_1(t) := \sum_j e^{-it\bar{V}''m^{-1/2}}(\gamma_j^r + i\gamma_j^i)\nu_j',$$

based on the orthonormal eigenvectors  $\{\nu_k'\}$  in (7), and for a given  $k$  define  $\varphi_2(t) := \sum_{j \neq k} e^{-it\bar{V}''m^{-1/2}}(\gamma_j^r + i\gamma_j^i)\nu_j'$ , that is  $\epsilon v(t) = -e^{-it\omega_k m^{-1/2}}(\gamma_k^r + i\gamma_k^i)\nu_k'$ , so that  $Z_1 = (X_1, P_1)$  is the path corresponding to  $\varphi_1$  and  $Z_2 = (X_2, P_2)$  corresponds to  $\varphi_2$  where  $\gamma_k\nu_k'$  is removed from the sum in  $\varphi_1$ . For any bounded and differentiable function  $h : \mathbb{R}^{2N} \rightarrow \mathbb{C}^n$  the perturbation property (47), with  $\varphi_0 = \sum_k \gamma_k\nu_k'$ , implies

$$\begin{aligned}
&\mathbb{E}[\langle e^{-it\bar{V}''m^{-1/2}}\varphi_0, h(Z_1(t)) \rangle] \\
&= \sum_k \mathbb{E}[\underbrace{\gamma_k^* \langle \nu_k', e^{-it\bar{V}''m^{-1/2}}h(Z_1(t)) \rangle}_{=: h_k(Z_1(t))}] \\
&= \sum_k \mathbb{E}[\gamma_k^* (h_k(Z_2) + \int_0^1 \nabla h_k(\sigma Z_2 + (1-\sigma)Z_1) d\sigma \\
&\quad \cdot \sum_\ell \int_0^t G_{\cdot P_\ell}(t, s) \text{Re}\langle e^{-is\omega_k m^{-1/2}} \gamma_k \nu_k', \bar{V}'' \partial_{X_\ell} a \rangle ds)] \\
(52) \quad &= \sum_k \underbrace{\mathbb{E}[\gamma_k^* h_k(Z_2)]}_{=\mathbb{E}[\gamma_k^*] \mathbb{E}[(h_k(Z_2))]=0} + \sum_k \mathbb{E}[\gamma_k^* \int_0^1 \nabla h_k(\sigma Z_2 + (1-\sigma)Z_1) d\sigma \\
&\quad \cdot \sum_\ell \int_0^t G_{\cdot P_\ell}(t, s) \text{Re}\langle e^{-is\omega_k m^{-1/2}} \gamma_k \nu_k', \bar{V}'' \partial_{X_\ell} a \rangle ds] \\
&= \sum_k \mathbb{E}[\gamma_k^* \nabla h_k(Z')] \cdot \sum_\ell \int_0^t G_{\cdot P_\ell}(t, s) \text{Re}\langle e^{-is\omega_k m^{-1/2}} \gamma_k \nu_k', \bar{V}'' \partial_{X_\ell} a \rangle ds],
\end{aligned}$$

where  $Z'$  is between  $Z_1(t)$  and  $Z_2(t)$  and satisfies

$$\nabla h(Z'(t)) = \int_0^1 \nabla h(Z_2(t) + \sigma(Z_1(t) - Z_2(t))) d\sigma.$$

We will use that the difference between  $Z_1$  and  $Z_2$  is small, namely

$$\begin{aligned}
 \Delta Z(t) &:= Z_2(t) - Z_1(t) = \sum_{\ell} \int_0^t G_{\cdot P_{\ell}}(t, s) \operatorname{Re} \langle e^{-is\omega_k m^{-1/2}} \gamma_k \nu'_k, \bar{V}'' \partial_{X_{\ell}} a \rangle ds \\
 (53) \qquad &= \sum_{\ell} \int_0^t G_{\cdot P_{\ell}}(t, s) \frac{T^{1/2}}{\omega_k n^{1/2}} \operatorname{Re} (e^{-is\omega_k m^{-1/2}} \xi_k \beta_{k,\ell}) ds,
 \end{aligned}$$

where  $\xi_k = \omega_k T^{-1/2} \gamma_k = \xi_{k,r} + i\xi_{k,i}$ , with  $\xi_{k,r}$  and  $\xi_{k,i}$  independent and standard normal distributed with mean zero and variance one. The eigenvalue representation (20) and (19) show that  $\sqrt{n} \omega_k \rightarrow \infty$  as  $n \rightarrow \infty$ . Consequently we have  $|Z_2 - Z_1| \rightarrow 0$  as  $n \rightarrow \infty$ , uniformly for all realizations.

*Step 3.* The dependence between  $\partial_P u(X_t, P_t, t)$  and  $\operatorname{Re} \langle e^{-it\bar{V}''/\sqrt{m}} \varphi_0, \bar{V}'' \nabla a \rangle$  from the initial data  $\varphi_0$  with  $Z' = (X', P')$  can by (52) and (34) be written

$$\begin{aligned}
 &\mathbb{E}[\langle \operatorname{Re}(e^{-it\sqrt{\bar{V}''}/\sqrt{m}} \varphi_0), \bar{V}'' \nabla a \cdot \nabla_P u(X_t, P_t, t) \rangle] \\
 &= \sum_{k,\ell,\ell',\ell''} \mathbb{E} \left[ \langle \underbrace{\operatorname{Re}(e^{-it\sqrt{\bar{V}''}/\sqrt{m}} \gamma_k \nu'_k)}_{=: S_{t_0}}, \bar{V}'' \partial_{X_{\ell}} a \rangle \right. \\
 &\quad \times \int_0^t \underbrace{\left( D_{P_{\ell'}, P_{\ell}}^2 u(X'_t, P'_t, t) G_{P_{\ell'}, P_{\ell''}}(t, s) + D_{X_{\ell'}, P_{\ell}}^2 u(X'_t, P'_t, t) G_{X_{\ell'}, P_{\ell''}}(t, s) \right)}_{=: U_{\ell,\ell',\ell''}(X_t, P_t, G, t, s)} \\
 &\quad \left. \times \langle \operatorname{Re}(e^{-is\sqrt{\bar{V}''}/\sqrt{m}} \gamma_k \nu'_k), \bar{V}'' \partial_{X_{\ell''}} a \rangle ds \right]
 \end{aligned}$$

so that by (14)

$$\begin{aligned}
 &\mathbb{E}[\langle \operatorname{Re}(e^{-it\sqrt{\bar{V}''}/\sqrt{m}} \varphi_0), \bar{V}'' \nabla a \cdot \nabla_P u(X_t, P_t, t) \rangle] \\
 &= \sum_{k,\ell,\ell',\ell''} \operatorname{Re} \left( e^{it\omega_k m^{-1/2}} \frac{T^{1/2} \beta_{k,\ell}}{\omega_k n^{1/2}} \right) \int_0^t \mathbb{E}[U_{\ell,\ell',\ell''}(X'_t, P'_t, G, t, s) |\xi_k^r|^2] \operatorname{Re}(\epsilon_{k,\ell''}(s)) ds \\
 &\quad \underbrace{\hspace{10em}}_{=: \epsilon_{k,\ell}(t)} \\
 &+ \sum_{k,\ell,\ell',\ell''} \operatorname{Im}(\epsilon_{k,\ell}(t)) \int_0^t \mathbb{E}[U_{\ell,\ell',\ell''}(X'_t, P'_t, G, t, s) |\xi_k^i|^2] \operatorname{Im}(\epsilon_{k,\ell''}(s)) ds \\
 &- \sum_{k,\ell,\ell',\ell''} \operatorname{Im}(\epsilon_{k,\ell}(t)) \int_0^t \mathbb{E}[U_{\ell,\ell',\ell''}(X'_t, P'_t, G, t, s) \xi_k^r \xi_k^i] \operatorname{Re}(\epsilon_{k,\ell''}(s)) ds \\
 &- \sum_{k,\ell,\ell',\ell''} \operatorname{Re}(\epsilon_{k,\ell}(t)) \int_0^t \mathbb{E}[U_{\ell,\ell',\ell''}(X'_t, P'_t, G, t, s) \xi_k^r \xi_k^i] \operatorname{Im}(\epsilon_{k,\ell''}(s)) ds.
 \end{aligned}$$

To determine the expected value  $\mathbb{E}[U_{\ell,\ell',\ell''}(X'_t, P'_t, G, t, s) \xi_k^r \xi_k^i]$  we use  $Z_2 = (X_2, P_2)$  in (47) based on  $\varphi_2$  and the Green's function

$$G_2(t, s) = \begin{bmatrix} G_{2,XX}(t, s) & G_{2,XP}(t, s) \\ G_{2,PX}(t, s) & G_{2,PP}(t, s) \end{bmatrix} \in \mathbb{R}^{2N \times 2N},$$

based on  $X_2$ , that is for  $t \geq s$  defined by

$$\begin{aligned} \partial_t G_{2, Xy}(t, s) &= G_{2, Py}(t, s), \\ \partial_t G_{2, Py}(t, s) &= -D^2 \lambda(X_2(t)) G_{2, Xy} \\ &\quad - \int_s^t \langle \bar{V}'' \cos\left(\frac{(t-r)\bar{V}''^{1/2}}{m^{1/2}}\right) \nabla a \cdot G_{2, Py}(r, s), \nabla a \rangle dr, \quad y = X, P, \\ G_2(s, s) &= \begin{bmatrix} \mathbf{I} & 0 \\ 0 & \mathbf{I} \end{bmatrix}. \end{aligned}$$

The difference of the two Green's functions satisfy by (47) the perturbation representation

$$\begin{aligned} G(t, s) - G_2(t, s) &= \int_s^t G(t, r) \begin{bmatrix} 0 & 0 \\ D^2 \lambda(X_2(r)) - \int_0^1 D^2 \lambda(\tau X_1(r) + (1-\tau)X_2(r)) d\tau & 0 \end{bmatrix} G_2(r, s) dr \\ &= \int_s^t G(t, r) \begin{bmatrix} 0 & 0 \\ \int_0^1 \int_0^1 D^3 \lambda(\tau X_2(r) + \tau \sigma \Delta X(r)) \tau \Delta X(r) d\tau d\sigma & 0 \end{bmatrix} G_2(r, s) dr. \end{aligned}$$

The processes  $Z_2$  and  $G_2$  do not depend on  $\xi_k$ . The expected value can therefore be evaluated using the Jacobian  $U' = DU$ , with respect to  $Z$  and  $G$ , and the small perturbation  $\Delta Z$  in the path from (53) as

$$\begin{aligned} &\mathbb{E}[U_{\ell, \ell', \ell''}(X'_t, P'_t, G, t, s) \xi_k^r \xi_k^i] \\ &= \mathbb{E}[U_{\ell, \ell', \ell''}(Z_2(t), G_2, t, s) \xi_k^r \xi_k^i] \\ &\quad + \mathbb{E}\left[\int_0^1 \int_0^1 U'_{\ell, \ell', \ell''}(Z_2(t) + \sigma \tau(Z_1(t) - Z_2(t)), G_2 + \tau(G - G_2), t, s) dr \right. \\ &\quad \left. \times \xi_k^r \xi_k^i \begin{bmatrix} \sigma(Z_1(t) - Z_2(t)) \\ G - G_2 \end{bmatrix} d\sigma\right] \\ &= \mathbb{E}[U_{\ell, \ell', \ell''}(Z_2(t), t, s)] \underbrace{\mathbb{E}[\xi_k^r \xi_k^i]}_{=0} + \mathcal{O}\left(\frac{1}{n^{1/2} \eta_n}\right) \end{aligned}$$

with analogous splittings for

$$U_{\ell, \ell', \ell''}(X'_t, P'_t, G, t, s) \xi_k^i \xi_k^i \quad \text{and} \quad U_{\ell, \ell', \ell''}(X'_t, P'_t, G, t, s) \xi_k^r \xi_k^r,$$

based on  $\mathbb{E}[\xi_k^r \xi_k^r] = \mathbb{E}[\xi_k^i \xi_k^i] = 1$ . Dominated convergence, using the assumption  $n^{1/2} \eta_n \rightarrow \infty$  in (19) as  $n \rightarrow \infty$ , implies therefore

$$\begin{aligned} &\lim_{\bar{n} \rightarrow \infty} \mathbb{E}[\langle \text{Re}(e^{-it\sqrt{\bar{V}''}/\sqrt{m}} \varphi_0), \bar{V}'' \nabla a \cdot \nabla_P u(X_t, P_t, t) \rangle] \\ &= \lim_{\bar{n} \rightarrow \infty} \sum_{k, \ell, \ell', \ell''} \text{Re}(\epsilon_{k, \ell}(t)) \int_0^t \mathbb{E}[U_{\ell, \ell', \ell''}(X_t, P_t, G, t, s)] \text{Re}(\epsilon_{k, \ell''}(s)) ds \\ &\quad + \lim_{\bar{n} \rightarrow \infty} \sum_{k, \ell, \ell', \ell''} \text{Im}(\epsilon_{k, \ell}(t)) \int_0^t \mathbb{E}[U_{\ell, \ell', \ell''}(X_t, P_t, G, t, s)] \text{Im}(\epsilon_{k, \ell''}(s)) ds \\ &= \lim_{\bar{n} \rightarrow \infty} \sum_{k, \ell, \ell', \ell''} \int_0^t \text{Re}(\epsilon_{k, \ell}^*(t) \epsilon_{k, \ell''}(s)) \mathbb{E}[U_{\ell, \ell', \ell''}(X_t, P_t, G, t, s)] ds, \end{aligned}$$



which shows that  $(X_t, P_t)$  in the limit becomes independent of the small perturbation caused by  $\langle \gamma_k \nu'_k, \bar{V}'' \nabla a \rangle$ . We have

$$\begin{aligned} \sum_k \operatorname{Re}(\epsilon_{k,\ell}^*(t) \epsilon_{k,\ell''}(s)) &= T \operatorname{Re} \left( \sum_k \langle \nu'_k, e^{i(t-s)\bar{V}''/\sqrt{m}} \partial_{X_\ell} a \rangle \langle \nu'_k, \bar{V}'' \partial_{X_{\ell''}} a \rangle \right) \\ &= T \langle \cos((t-s)\bar{V}''/\sqrt{m}) \partial_{X_\ell} a, \bar{V}'' \partial_{X_{\ell''}} a \rangle, \end{aligned}$$

and we obtain then as in the proof of (35)

$$\begin{aligned} & \lim_{\bar{n} \rightarrow \infty} \sum_{\ell, \ell', \ell''} \mathbb{E} \left[ \sum_k \operatorname{Re} \langle S_{t0}(\gamma_k^r + i\gamma_k^i) \nu'_k, \bar{V}'' \partial_{X_\ell} a \rangle \right. \\ & \quad \times \left( D_{P_{\ell'}, P_\ell}^2 u \int_0^t G_{P_{\ell'}, P_{\ell''}}(t, s) \operatorname{Re} \langle S_{s0}(\gamma_k^r + i\gamma_k^i) \nu'_k, \bar{V}'' \partial_{\ell''} a \rangle ds \right. \\ & \quad \left. \left. + D_{X_{\ell'}, P_\ell}^2 u \int_0^t G_{X_{\ell'}, P_{\ell''}}(t, s) \operatorname{Re} \langle S_{s0}(\gamma_k^r + i\gamma_k^i) \nu'_k, \bar{V}'' \partial_{\ell''} a \rangle ds \right) \right] \\ &= T \lim_{\bar{n} \rightarrow \infty} \sum_{\ell, \ell', \ell''} \mathbb{E} \left[ \int_0^t (D_{P_{\ell'}, P_\ell}^2 u G_{P_{\ell'}, P_{\ell''}}(t, s) + D_{X_{\ell'}, P_\ell}^2 u G_{X_{\ell'}, P_{\ell''}}(t, s)) \right. \\ & \quad \left. \times \langle \cos((t-s)\sqrt{\bar{V}''}/\sqrt{m}) \partial_{X_\ell} a, \bar{V}'' \partial_{X_{\ell''}} a \rangle ds \right] \\ &= m^{1/2} T \sum_{\ell, \ell', \ell''} \mathbb{E} \left[ \int_0^{t/\sqrt{m}} (D_{P_{\ell'}, P_\ell}^2 u(X_t, P_t, t) G_{P_{\ell'}, P_{\ell''}}(t, t - \sqrt{m}\tau) \right. \\ & \quad \left. + D_{X_{\ell'}, P_\ell}^2 u(X_t, P_t, t) G_{X_{\ell'}, P_{\ell''}}(t, t - \sqrt{m}\tau)) \langle \cos(\tau\sqrt{\bar{V}''}) \partial_{X_\ell} a, \bar{V}'' \partial_{X_{\ell''}} a \rangle d\tau \right]. \end{aligned}$$

Lemma 3.1 with  $G(t, t - \sqrt{m}\tau) = G(t - \sqrt{m}\tau, t - \sqrt{m}\tau) + \int_{t - \sqrt{m}\tau}^t \partial_r G(r, t - \sqrt{m}\tau) dr$  replacing

$$(X(t - \sqrt{m}\tau), P(t - \sqrt{m}\tau)) = ((X(t)P(t)) - \int_{t - \sqrt{m}\tau}^t (\dot{X}(s), \dot{P}(s)) ds),$$

using also (48),  $G_{PP}(t - \sqrt{m}\tau, t - \sqrt{m}\tau) = I$  and  $G_{XP}(t - \sqrt{m}\tau, t - \sqrt{m}\tau) = 0$ , verifies (43):

$$\begin{aligned} & m^{1/2} T \sum_{\ell, \ell', \ell''} \mathbb{E} \left[ \int_0^{t/\sqrt{m}} (D_{P_{\ell'}, P_\ell}^2 u(X_t, P_t, t) G_{P_{\ell'}, P_{\ell''}}(t, t - \sqrt{m}\tau) \right. \\ & \quad \left. + D_{X_{\ell'}, P_\ell}^2 u(X_t, P_t, t) G_{X_{\ell'}, P_{\ell''}}(t, t - \sqrt{m}\tau)) \langle \cos(\tau\sqrt{\bar{V}''}) \partial_{X_\ell} a, \bar{V}'' \partial_{X_{\ell''}} a \rangle d\tau \right] \\ &= m^{1/2} T \mathbb{E} [D_{PP}^2 u(X_t, P_t, t) : \kappa] + \mathcal{O}(m \log m^{-1}). \end{aligned}$$

□

4. ANALYSIS OF THE GENERALIZED LANGEVIN EQUATION FOR  $\chi \ll 1$ 

In this section we study a time scale separation for system particles and fast heat bath particles due to a stiff heat bath obtained by changing the scaling to

$$\begin{aligned}
\bar{V}'' &= \chi^{-1} \tilde{V}'', \\
a(X) &= \chi^\delta \tilde{a}(X), \\
(54) \quad \varphi_0 &= \sum_k \gamma_k \nu'_k = \chi^{1/2} \sum_k \tilde{\gamma}_k \nu'_k = \chi^{1/2} \tilde{\varphi}_0, \\
\tilde{\gamma}_k &\sim N(0, T/\tilde{\omega}_k^2), \\
\tilde{\omega}_k^2 &\text{ are the eigenvalues of } \tilde{V}'',
\end{aligned}$$

and assume that

$$(55) \quad m \text{ and the elements of } \tilde{V}'' \text{ and } \tilde{a} \text{ are of size one while } \chi \ll 1.$$

The nonlinear generalized Langevin equation then becomes

$$\begin{aligned}
\ddot{X}_t &= -\nabla\lambda(X_t) - \chi^{2\delta-1} \int_0^t \langle \tilde{V}'' \cos\left(\frac{(t-s)\tilde{V}''^{1/2}}{(\chi m)^{1/2}}\right) \dot{a}(X_s), \nabla\tilde{a}(X_t) \rangle ds \\
&\quad + \chi^{\delta-1/2} \text{Re} \langle \tilde{V}'' e^{-i\tilde{V}''^{1/2}(\chi m)^{-1/2}t} \tilde{\varphi}_0, \nabla\tilde{a}(X_t) \rangle.
\end{aligned}$$

The analysis in Section 3 can be applied by replacing  $m$  by  $\chi m$ ;  $\bar{V}''$  by  $\tilde{V}''$ ; and  $a$  by  $\tilde{a}$  and we obtain

**Theorem 4.1.** *Let  $m_0 := \chi^{2\delta-1/2} m^{1/2}$  with  $\delta > 1/4$  and assume that (54)-(55) hold together with the assumptions in Theorem 3.4, then the Langevin dynamics*

$$\begin{aligned}
dX_L(t) &= P_L(t) dt \\
dP_L(t) &= -\nabla\lambda(X_L(t)) dt - m_0 \kappa P_L(t) dt + (2m_0 \kappa T)^{1/2} dW(t), \\
X_L(0) &= X(0), \\
P_L(0) &= P(0)
\end{aligned}$$

approximates the Hamiltonian dynamics (6) and (10), with the error estimate

$$\begin{aligned}
&\left| \mathbb{E}[g(X_{t_*}, P_{t_*}) \mid X_0, P_0] - \mathbb{E}[g(X_L(t_*), P_L(t_*)) \mid (X_L(0), P_L(0)) = (X_0, P_0)] \right| \\
&= \mathcal{O}(m_0 \chi^{1/2} \log \chi^{-1}) = \mathcal{O}(\chi^{2\delta} \log \chi^{-1}),
\end{aligned}$$

where the friction matrix is determined by the force  $\tilde{F}_{\ell j} = \lim_{n \rightarrow \infty} (\tilde{V}'' \partial_{X_\ell} \tilde{a})(j)$  as

$$(56) \quad \kappa_{\ell\ell'} = \frac{1}{4\pi c^3} \left( \sum_{j \in E_\infty} \tilde{F}_{\ell j} \right) \left( \sum_{j \in E_\infty} \tilde{F}_{\ell' j} \right).$$

## 5. MOLECULAR DYNAMICS APPROXIMATION OF A QUANTUM SYSTEM

The purpose of this section is to present a molecular dynamics approximation for observables of a quantum particle system consisting of nuclei and electrons coupled to a heat bath. The observables may include correlations in time. The first subsection provides background to quantum observables approximated by molecular dynamics in the canonical ensemble. The next subsection combines these quantum approximation results of with the classical Langevin approximation in Theorems 3.4 and 4.1.

**5.1. Canonical quantum observables approximated by molecular dynamics.** The quantum formulation is based on wave functions  $\Phi : \mathbb{R}^N \times \mathbb{R}^n \rightarrow \mathbb{C}^d$  and the Hamiltonian

$$-\frac{M_s^{-1}}{2}\mathbf{I}\Delta_X - \frac{M_b^{-1}}{2}\mathbf{I}\Delta_x + V(X) + V_b(x, X),$$

where  $X \in \mathbb{R}^N$  and  $x \in \mathbb{R}^n$  are the nuclei coordinates of the system and heat bath positions, respectively, and  $M_s$  and  $M_b$  are the diagonal matrices of the mass of the system nuclei and heat bath nuclei, respectively, measured in units of the electron mass. The functions  $V : \mathbb{R}^N \rightarrow \mathbb{C}^{d^2}$  and  $V_b : \mathbb{R}^n \times \mathbb{R}^N \rightarrow \mathbb{C}^{d^2}$  are finite difference approximations of the electron kinetic energy and nuclei–nuclei, nuclei–electron and electron–electron interactions, related to the system and the heat bath. The matrix  $\mathbf{I}$  is the identity on  $\mathbb{C}^d$ . This simplification to replace the Laplacians for the electron kinetic energy by difference approximations makes it easier to derive the classical limit. Another simplification is to change coordinates  $M^{1/2}\bar{X} = M_s^{1/2}X$  and  $M^{1/2}\bar{x} = M_b^{1/2}x$  and let  $\tilde{x} = (\bar{X}, \bar{x}) \in \mathbb{R}^{N+n}$ , where  $M \gg 1$  is a reference nuclei–electron mass ratio. In these coordinates the Hamiltonian takes the form

$$\hat{H} = -\frac{1}{2M}\mathbf{I}\Delta_{\tilde{x}} + v(\tilde{x}),$$

where  $v(\tilde{x}) := V(M_s^{-1/2}M^{1/2}\bar{X}) + V_b(M_b^{-1/2}M^{1/2}\bar{x}, M_s^{-1/2}M^{1/2}\bar{X})$ . We will use the eigenvalues  $\lambda_k(\tilde{x}) \in \mathbb{R}$  and eigenvectors  $\psi_k(\tilde{x})$  of the Hermitian matrix  $v(\tilde{x})$  defined by

$$v(\tilde{x})\psi_k(\tilde{x}) = \lambda_k(\tilde{x})\psi_k(\tilde{x}).$$

We assume that the eigenvalues satisfy

$$(57) \quad \begin{aligned} \lambda_1(\tilde{x}) &< \lambda_2(\tilde{x}) < \dots < \lambda_d(\tilde{x}), \\ \lambda_1(\tilde{x}) &\rightarrow \infty \text{ as } |\tilde{x}| \rightarrow \infty. \end{aligned}$$

The first assumption is in order to have differentiable eigenvectors and the second condition implies that the spectrum of  $\hat{H}$  is discrete, see [4].

The aim here is to study canonical quantum observables, including correlations in time, namely

$$\text{trace}(\hat{A}_\tau \hat{C}_0) = \sum_{n=1}^{\infty} (\Phi_n, \hat{A}_\tau \hat{C}_0 \Phi_n),$$

where  $\{\Phi_n\}_{n=1}^{\infty}$  is a normalized basis of  $L^2(d\tilde{x})$ , e.g. the set of normalized eigenfunctions to  $\hat{H}$  and  $(f, g) := \int_{\mathbb{R}^{N+n}} f^*(\tilde{x})g(\tilde{x})d\tilde{x}$ . An operator  $\hat{B}$  is the Weyl quantization that maps  $L^2(\mathbb{R}^{N+n})$  to  $[L^2(\mathbb{R}^{N+n})]^d$  and is defined, from a  $d \times d$  matrix valued symbol  $B : \mathbb{R}^{N+n} \rightarrow \mathbb{C}^{d^2}$  in the Schwartz class, by

$$\hat{B}\Phi(\tilde{x}) = \left(\frac{M^{1/2}}{2\pi}\right)^{N+n} \int_{\mathbb{R}^{2(N+n)}} e^{iM^{1/2}(\tilde{x}-y)\cdot\tilde{p}} B\left(\frac{\tilde{x}+y}{2}, \tilde{p}\right)\Phi(y)d\tilde{p}dy.$$

For instance, we have  $\widehat{\frac{|\tilde{p}|^2}{2}} + v(\tilde{x}) = \hat{H}$ . The time dependent operator  $\hat{B}_\tau$  is defined by

$$\hat{B}_\tau := e^{i\tau M^{1/2}\hat{H}} \hat{B} e^{-i\tau M^{1/2}\hat{H}}, \tau \in \mathbb{R},$$

which implies the von Neumann-Heisenberg equation

$$(58) \quad \frac{d}{d\tau} \hat{B}_\tau = iM^{1/2}[\hat{H}, \hat{B}_\tau]$$

where  $[\hat{H}, \hat{B}_\tau] := \hat{H}\hat{B}_\tau - \hat{B}_\tau\hat{H}$  is the commutator. The example of the observable for the diffusion constant

$$\frac{1}{6\tau} \frac{3}{N+n} \sum_{k=1}^{(N+n)/3} |\tilde{x}_k(\tau) - \tilde{x}_k(0)|^2 = \frac{1}{2(N+n)\tau} (|\tilde{x}(\tau)|^2 + |\tilde{x}(0)|^2 - 2\tilde{x}(\tau) \cdot \tilde{x}(0))$$

uses the time-correlation  $\hat{x}(\tau) \cdot \hat{x}(0)$  where  $\hat{A}_\tau = \hat{x}_\tau \mathbf{I}$  and  $\hat{C}_0 = \hat{x}_0 \mathbf{I}$  and

$$\hat{x}_\tau \cdot \hat{x}_0 = \sum_{k=1}^{(N+n)/3} \sum_{j=1}^3 e^{i\tau M^{1/2} \hat{H}} \hat{x}_{k_j} e^{-i\tau M^{1/2} \hat{H}} \hat{x}_{k_j}.$$

A main tool to determine the classical limit is to diagonalize (58), which is based on the following composition of Weyl quantizations: the symbol  $C$  for the product of two Weyl operators  $\hat{A}\hat{B} = \hat{C}$  is determined by

$$(59) \quad C(\tilde{x}, \tilde{p}) = e^{\frac{i}{2M^{1/2}} (\nabla_{\tilde{x}'} \cdot \nabla_{\tilde{p}} - \nabla_{\tilde{x}} \cdot \nabla_{\tilde{p}'})} A(\tilde{x}, \tilde{p}) B(\tilde{x}', \tilde{p}') \Big|_{\substack{\tilde{x} = \tilde{x}' \\ \tilde{p} = \tilde{p}'}} =: (A \# B)(\tilde{x}, \tilde{p}),$$

see [29]. Assume that  $\Psi : \mathbb{R}^{N+n} \rightarrow \mathbb{C}^{d^2}$  and  $\Psi(\tilde{x})$  is any unitary matrix with the Hermitian transpose  $\Psi^*(\tilde{x})$  and define  $\bar{A} : \mathbb{R}^{N+n} \times [0, \infty) \rightarrow \mathbb{C}^{d^2}$  by

$$\hat{A}_\tau = \hat{\Psi}(\tilde{x}) \hat{A}_\tau \hat{\Psi}^*(\tilde{x})$$

so that

$$\hat{\bar{A}}_\tau = \hat{\Psi}^*(\tilde{x}) \hat{A}_\tau \hat{\Psi}(\tilde{x}).$$

Then

$$[\hat{H}, \hat{A}_\tau] = \hat{\Psi}[\hat{\Psi}^* \hat{H} \hat{\Psi}, \hat{A}_\tau] \hat{\Psi}^*$$

and consequently

$$\partial_\tau \hat{\bar{A}}_\tau = iM^{1/2} [\hat{\Psi}^* \hat{H} \hat{\Psi}, \hat{\bar{A}}_\tau].$$

The composition rule (59) implies  $\hat{\Psi}^* \hat{H} \hat{\Psi} = (\Psi^* \# H \# \Psi)^\wedge$  and  $\bar{A}_\tau = \Psi^* \# A_\tau \# \Psi$ . The next step is to determine  $\Psi$  so that

$$\bar{H} := \Psi^* \# H \# \Psi$$

is almost diagonal. Having  $\bar{H}$  diagonal implies that  $\hat{H}$  is diagonal and then  $\hat{A}$  remains diagonal if it initially were diagonal, since then

$$\frac{d}{d\tau} \hat{A}_{jk}(\tau) = iM^{1/2} (\hat{H}_{jj} \hat{A}_{jk}(\tau) - \hat{A}_{jk}(\tau) \hat{H}_{kk}) = 0, \quad \text{for } j \neq k.$$

The composition rule (59) with

$$H(\tilde{x}, \tilde{p}) = \frac{|\tilde{p}|^2}{2} \mathbf{I} + v(\tilde{x})$$

implies that

$$\begin{aligned} \bar{H} &= \Psi^* \# H \# \Psi \\ &= \frac{|\tilde{p}|^2}{2} \mathbf{I} + \Psi^* v \Psi + \frac{1}{4M} \nabla \Psi^* \cdot \nabla \Psi \\ &= \Psi^* \left( \frac{|\tilde{p}|^2}{2} \mathbf{I} + v + \frac{1}{4M} \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^* \right) \Psi, \end{aligned}$$

as verified in [10, Lemma 3.1]. Therefore, the aim is to choose the unitary matrix  $\Psi$  so that it becomes an approximate solution to the nonlinear eigenvalue problem

$$\left( v + \frac{1}{4M} \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^* \right) \Psi = \Psi \bar{\Lambda}$$

in the sense that

$$(60) \quad \left(v + \frac{1}{4M} \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^*\right) \Psi = \Psi \bar{\Lambda} + \mathcal{O}(M^{-2})$$

where  $\bar{\Lambda} : \mathbb{R}^{N+n} \rightarrow \mathbb{C}^{d \times d}$  is diagonal, that is

$$\bar{\Lambda}_{jk}(\tilde{x}) = \begin{cases} 0 & j \neq k \\ \bar{\lambda}_j(\tilde{x}) & j = k \end{cases}.$$

Such a solution  $\Psi$  then implies

$$\bar{H}(\tilde{x}, \tilde{p}) = \frac{|\tilde{p}|^2}{2} \mathbf{I} + \bar{\Lambda}(\tilde{x}) + r_0(\tilde{x}),$$

where the remainder satisfies  $\|r_0\|_{L^\infty(\mathbb{R}^{N+n})} = \mathcal{O}(M^{-2})$ . A solution,  $\Psi$ , to this nonlinear eigenvalue problem is an  $\mathcal{O}(M^{-1})$  perturbation of the eigenvectors to  $v(\tilde{x})$  provided the eigenvalues do not cross and  $M$  is sufficiently large. The work [10, (3.18)] shows that (60) has a solution  $\Psi$ , if  $v$  is twice differentiable, the eigenvalues of  $v$  are distinct and  $M$  is sufficiently large.

The canonical ensemble is typically based on  $\text{trace}(\hat{C}e^{-\hat{H}/T})/\text{trace}(e^{-\hat{H}/T})$ . We will instead use the related  $\text{trace}(\hat{C}\widehat{e^{-\bar{H}/T}})/\text{trace}(\widehat{e^{-\bar{H}/T}})$ . If the density operators  $e^{-\hat{H}/T}$  and  $\widehat{e^{-\bar{H}/T}}$  would differ only little it would not matter which one we use as a reference. Since we do not know if this difference is small in the case of a large number of particles, we may ask which density operator to use. The density operator  $\hat{\rho}_q = e^{-\hat{H}/T}$  is a time-independent solution to the quantum Liouville-von Neumann equation

$$\partial_t \hat{\rho}_t = iM^{1/2}[\hat{\rho}_t, \hat{H}]$$

while the classical Gibbs density  $e^{-\bar{H}/T}$  is a time-independent solution to the classical Liouville equation

$$\partial_t \bar{\rho}_t = -\{\bar{\rho}_t, \bar{H}\},$$

with the Poisson bracket in the right hand side. The corresponding density matrix symbol  $\rho_q$  is not a time-independent solution to the classical Liouville equation, since

$$0 = iM^{1/2}(\rho_q \# \bar{H} - \bar{H} \# \rho_q) \neq \{\rho_q, \bar{H}\},$$

and the classical Gibbs density is not a time-independent solution to the quantum Liouville-von Neumann equation, since

$$iM^{1/2}(e^{-\bar{H}/T} \# \bar{H} - \bar{H} \# e^{-\bar{H}/T}) \neq \{e^{-\bar{H}/T}, \bar{H}\} = 0.$$

However, it is shown in [10] that a solution to the quantum Liouville equation  $\hat{\rho}_t$  with initial data  $\rho_0 = e^{-\bar{H}/T}$  generates only a small time dependent perturbation on observables up to time  $t < M$ , which motivates our use of  $\widehat{e^{-\bar{H}/T}}$ .

The following result for approximating non equilibrium quantum observables by classical molecular dynamics observables is proved in [10].

**Theorem 5.1.** *Assume that  $v$  satisfies (57), the  $d \times d$  matrices  $\bar{A} \equiv \bar{A}_0$  and  $\bar{B}$  are diagonal, the  $d \times d$  matrix valued Hamiltonian  $H$  has distinct eigenvalues, and that*

there is a constant  $C$  such that

$$\begin{aligned} \sum_{|\alpha| \leq 2} \|\partial_{\tilde{x}}^{\alpha} \psi_k\|_{L^{\infty}(\mathbb{R}^N)} &\leq C, \quad k = 1, \dots, d, \\ \max_i \sum_{|\alpha| \leq 3} \|\partial_{\tilde{x}}^{\alpha} \partial_{\tilde{x}_i} \bar{\lambda}_j\|_{L^{\infty}(\mathbb{R}^{N+n})} &\leq C, \\ \sum_{|\alpha| \leq 3} \|\partial_{\tilde{z}}^{\alpha} \bar{A}_{jj}\|_{L^2(\mathbb{R}^{2(N+n)})} &\leq C, \\ \|\bar{B}(\tilde{z})e^{-\bar{H}(\tilde{z})/T}\|_{L^2(\mathbb{R}^{2(N+n)})} &\leq C, \end{aligned}$$

then there is a constant  $C'$ , depending on  $C$ , such that the canonical ensemble average satisfies

$$\left| \frac{\text{trace}(\hat{A}_{\tau} \hat{\Psi}(\bar{B}e^{-\bar{H}/T}) \hat{\Psi}^*)}{\text{trace}(\hat{\Psi}e^{-\bar{H}/T} \hat{\Psi}^*)} - \sum_{j=1}^d \int_{\mathbb{R}^{2(N+n)}} \frac{\bar{A}_{jj}(\tilde{z}_{\tau}^j(\tilde{z}_0)) \bar{B}_{jj}(\tilde{z}_0) e^{-\bar{H}_{jj}(\tilde{z}_0)/T}}{\sum_{k=1}^d \int_{\mathbb{R}^{2(N+n)}} e^{-\bar{H}_{kk}(\tilde{z})/T} d\tilde{z}} d\tilde{z}_0 \right| \leq \frac{C'}{M},$$

where  $\tilde{z}_{\tau}^j = (\tilde{x}_{\tau}, \tilde{p}_{\tau})$  is the solution to the Hamiltonian system

$$\begin{aligned} \dot{\tilde{x}}_{\tau} &= \tilde{p}_{\tau} \\ \dot{\tilde{p}}_{\tau} &= -\nabla \bar{\lambda}_j(\tilde{x}_{\tau}), \quad \tau > 0, \end{aligned}$$

based on the Hamiltonian  $\bar{H}_{jj}(\tilde{x}, \tilde{p}) = |\tilde{p}|^2/2 + \bar{\lambda}_j(\tilde{x})$ , with initial data  $(\tilde{x}_0, \tilde{p}_0) = \tilde{z}_0 \in \mathbb{R}^{2(N+n)}$ .

**5.2. Langevin dynamics derived from quantum mechanics.** Assume that the potential  $V(X)$  has the eigenvalues  $\lambda_j(X)$  and eigenvectors  $\psi_j(X)$ ,  $j = 1, \dots, d$ . The eigenvalues of the potential  $v(\tilde{x}(X, x)) = V(X) + V_b(x, X)$  will to leading order in  $\|V_b(\cdot, X)\|$  be given by  $\lambda_j(X) + \psi_j^* V_b(x, X) \psi_j$ . We assume now that all coupling potentials  $\psi_j^* V_b(x, X) \psi_j$  satisfy the weak coupling assumptions (3) and (4), namely

$$\min_x \psi_j^*(X) V_b(x, X) \psi_j(X) = \psi_j^*(X) V_b(a_j(X), X) \psi_j(X) = 0$$

so that

$$\bar{\lambda}_j(\tilde{x}(x, X)) = \lambda_j(X) + \langle x - a_j(X), \bar{V}_j''(x - a_j(X)) \rangle$$

where  $\bar{V}_j'' = \psi_j^* V_{b_{xx}}'' \psi_j$  is a constant matrix as in (4) and each coupling  $\psi_j^* V_b \psi_j$  for  $j = 1, \dots, d$  yields one equilibrium position  $a_j(X)$  and one coupling matrix  $\bar{V}_j''$ . The eigenvalues of the Hamiltonian symbol

$$\left(\frac{M}{2} P \cdot M_s^{-1} P + \frac{M}{2} p \cdot M_b^{-1} p\right) \mathbf{I} + V(X) + V_b(x, X)$$

are then

$$\begin{aligned} \bar{H}_{jj}(X, P, x, p) &= \frac{M}{2} P \cdot M_s^{-1} P + \frac{M}{2} p \cdot M_b^{-1} p + \bar{\lambda}_j(\tilde{x}(x, X)) \\ &= \frac{M}{2} P \cdot M_s^{-1} P + \frac{M}{2} p \cdot M_b^{-1} p + \lambda_j(X) + \langle x - a_j(X), \bar{V}_j''(x - a_j(X)) \rangle. \end{aligned}$$

Let  $m$  be the mass ratio for a reference heat bath nuclei to a reference system nuclei. Theorems 3.4 and 4.1 show the classical dynamics provided by the Hamiltonians  $\bar{H}_{jj}$  are accurately approximated by the Langevin dynamics

$$\begin{aligned} dX_t &= MM_s^{-1} P_t dt, \\ dP_t &= -\nabla \lambda_j(X_t) dt - m^{1/2} \kappa^j M_s^{-1} P_t dt + \sqrt{2m^{1/2} \kappa^j T} dW_t, \end{aligned}$$

where  $\kappa_{\ell\ell'}^j = \frac{1}{4\pi c_j^3} \langle \bar{V}_j'' \partial_{X_\ell} a_j, \bar{V}_j'' \partial_{X_{\ell'}} a_j \rangle$ , for  $m \ll 1$ . The next step is to relate this approximation by Langevin dynamics also to quantum observables in the canonical ensemble. In particular we need to obtain the Gibbs distribution of the heat bath particles from the quantum observables in the canonical ensemble.

Define the probability,  $q_j$ , to be in electron state  $j$  as

$$(61) \quad q_j := \frac{\int_{\mathbb{R}^{2(N+n)}} e^{-\bar{H}_{jj}(\tilde{z})/T} d\tilde{z}}{\sum_{k=1}^d \int_{\mathbb{R}^{2(N+n)}} e^{-\bar{H}_{kk}(\tilde{z})/T} d\tilde{z}}, \quad j = 1, \dots, d,$$

then the molecular dynamics observable becomes a sum of observables in the different electron states with initial Gibbs distribution, namely

$$\begin{aligned} & \sum_{j=1}^d \int_{\mathbb{R}^{2(N+n)}} \frac{\bar{A}_{jj}(\tilde{z}_\tau^j(\tilde{z}_0)) \bar{B}_{jj}(\tilde{z}_0) e^{-\bar{H}_{jj}(\tilde{z}_0)/T}}{\sum_{k=1}^d \int_{\mathbb{R}^{2(N+n)}} e^{-\bar{H}_{kk}(\tilde{z})/T} d\tilde{z}} d\tilde{z}_0 \\ &= \sum_{j=1}^d q_j \int_{\mathbb{R}^{2(N+n)}} \frac{\bar{A}_{jj}(\tilde{z}_\tau^j(\tilde{z}_0)) \bar{B}_{jj}(\tilde{z}_0) e^{-\bar{H}_{jj}(\tilde{z}_0)/T}}{\int_{\mathbb{R}^{2(N+n)}} e^{-\bar{H}_{jj}(\tilde{z})/T} d\tilde{z}} d\tilde{z}_0. \end{aligned}$$

For instance if only the ground state matters we have  $q_1 = 1$  and  $q_k = 0$ ,  $k = 2, 3, 4, \dots, d$ .

We simplify by letting the system nuclei have the same mass  $M$  and the heat bath nuclei the same mass  $mM$ . Then the diagonalized Hamiltonian can by (5) be written as

$$\bar{H}_{jj}(\tilde{z}) = \frac{|P|^2}{2} + \lambda_j(X) + \frac{|p|^2}{2m} + \langle (x - a_j(X), \bar{V}_j''(x - a_j(X)) \rangle,$$

where  $\tilde{z} = (X, P, x, p) \in \mathbb{R}^N \times \mathbb{R}^N \times \mathbb{R}^n \times \mathbb{R}^n$ . Assume that the observables  $\bar{A}_{jj}$  and  $\bar{B}_{jj}$  only depend on the system coordinates  $X$  and  $P$ , then the classical molecular dynamics approximation of the canonical quantum observables in Theorem 5.1 satisfies

$$\begin{aligned} & \int_{\mathbb{R}^{2(N+n)}} q_j \bar{A}_{jj}(X_\tau^j(\tilde{z}_0), P_\tau^j(\tilde{z}_0)) \bar{B}_{jj}(X_0, P_0) \frac{e^{-\bar{H}_{jj}(\tilde{z}_0)/T}}{\int_{\mathbb{R}^{2(N+n)}} e^{-\bar{H}_{jj}(\tilde{z})/T} d\tilde{z}} d\tilde{z}_0 \\ &= \int_{\mathbb{R}^{2n}} \int_{\mathbb{R}^{2N}} q_j \bar{A}_{jj}(X_\tau^j(\tilde{z}_0), P_\tau^j(\tilde{z}_0)) \bar{B}_{jj}(X_0, P_0) \frac{e^{-(\frac{|P_0|^2}{2} + \lambda_j(X_0))/T}}{\int_{\mathbb{R}^{2N}} e^{-(\frac{|P|^2}{2} + \lambda_j(X))/T} dX dP} \\ & \quad \times \frac{e^{-(\frac{|p|^2}{2m} + \langle x - a_j(X_0), \bar{V}_j''(x - a_j(X_0)) \rangle / T}}{\int_{\mathbb{R}^{2n}} e^{-(\frac{|p|^2}{2m} + \langle x - a_j(X_0), \bar{V}_j''(x - a_k(X_0)) \rangle / T} dx dp} dX_0 dP_0 dx dp \\ &= \mathbb{E} \left[ \int_{\mathbb{R}^{2N}} q_j \bar{A}_{jj}(X_\tau^j(\tilde{z}_0), P_\tau^j(\tilde{z}_0)) \bar{B}_{jj}(X_0, P_0) \frac{e^{-(\frac{|P_0|^2}{2} + \lambda_j(X_0))/T}}{\int_{\mathbb{R}^{2N}} e^{-(\frac{|P|^2}{2} + \lambda_j(X))/T} dX dP} dX_0 dP_0 \right] \end{aligned}$$

where the expected value is with respect to the Gibbs measure

$$(62) \quad \frac{e^{-(\frac{|p|^2}{2m} + \langle x - a_j(X_0), \bar{V}_j''(x - a_j(X_0)) \rangle / T}}{\int_{\mathbb{R}^{2n}} e^{-(\frac{|p|^2}{2m} + \langle x - a_j(X_0), \bar{V}_j''(x - a_k(X_0)) \rangle / T} dx dp}$$

of the heat bath coordinates conditioned on the initial system coordinates. We note that the Gibbs measure (62) is the invariant measure used to sample the initial heat bath configurations in theorems 3.4 and 4.1. Therefore the combination of theorems 3.4, 4.1 and 5.1 show that canonical observables for a quantum system coupled

to a heat bath can be accurately approximated by Langevin dynamics, with the friction coefficient determined by (44) and (56), including several electron surfaces  $\lambda_j$ ,  $j = 1, \dots, d$ .

**Theorem 5.2.** *Suppose that the assumptions in Theorems 5.1 and (3.4 or 4.1) hold and the observables  $\bar{A}_{jj}(\cdot)$  and  $\bar{B}_{jj}(\cdot)$  depend only on the system coordinates  $(X_0, P_0)$ , then*

$$\begin{aligned} & \frac{\text{trace}(\hat{A}_\tau \hat{\Psi}(\widehat{\bar{B}e^{-\bar{H}/T}})\hat{\Psi}^*)}{\text{trace}(\hat{\Psi}e^{-\bar{H}/T}\hat{\Psi}^*)} = \frac{\text{trace}((\bar{A}_\tau(X, P))(\widehat{\bar{B}(X, P)e^{-\bar{H}/T}}))}{\text{trace}(e^{-\bar{H}/T})} \\ &= \sum_{j=1}^d \mathbb{E}[q_j \int_{\mathbb{R}^{2N}} \bar{A}_{jj}(X_\tau^j(X_0, P_0), P_\tau^j(X_0, P_0)) \bar{B}_{jj}(X_0, P_0) \\ & \quad \times \frac{e^{-(\frac{|P_0|^2}{2} + \lambda_j(X_0))/T}}{\int_{\mathbb{R}^{2N}} e^{-(\frac{|P|^2}{2} + \lambda_j(X))/T} dX dP} dX_0 dP_0] \\ & + \mathcal{O}(\bar{M}^{-1} + \bar{\chi}), \end{aligned}$$

where

$$\begin{aligned} (\bar{\chi}, \bar{m}, \bar{M}) &:= (m \log m^{-1}, m^{1/2}, mM) \text{ for } m \rightarrow 0^+ \text{ in Theorem 3.4 or} \\ (\bar{\chi}, \bar{m}, \bar{M}) &:= (\chi^{2\delta} \log \chi^{-1}, \chi^{2\delta-1/2} m^{1/2}, M) \text{ for } \chi \rightarrow 0^+ \text{ in Theorem 4.1,} \end{aligned}$$

and  $(X_t^j, P_t^j)$ , for  $t > 0$ , is the solution to the Langevin equation

$$\begin{aligned} dX_t^j &= P_t^j dt \\ dP_t^j &= -\nabla \lambda_j(X_t^j) dt - \bar{m} \kappa^j P_t^j dt + (2\bar{m} \kappa^j T)^{1/2} dW_t, \end{aligned}$$

with initial data  $(X_0^j, P_0^j) = (X_0, P_0)$ ,

$$\kappa_{\ell\ell'}^j = \frac{1}{4\pi c_j^3} \langle \bar{V}_j'' \partial_{X_\ell} a_j, \bar{V}_j'' \partial_{X_{\ell'}} a_j \rangle$$

and  $c_j$  set by the Jacobian determinant of heat bath states at zero frequency in (27). The probability  $q_j$  to be in electron state  $j$  is determined by (61) and the expected value is with respect to the Wiener process  $W$ , with  $N$  independent components.

## 6. NUMERICAL EXAMPLE

We consider a single heavy particle in  $\mathbb{R}^3$ , the nearest neighbour lattice interaction  $\bar{V}''$ , cf. (18),  $\lambda(X) = |X|^2/2$ ,  $c = 1$  and

$$\beta_\ell(\omega) = \mathbf{1}_{|\omega| \leq 1} \prod_{i=1}^3 \pi^{1/2} (4 - \omega_i^2)^{1/4} \quad \text{for all } \ell \in \{1, 2, 3\},$$

implying by (25) that

$$f(\omega, \ell, \ell') = \mathbf{1}_{|\omega| \leq 1} \quad \text{for all } \ell, \ell' \in \{1, 2, 3\}.$$

Since this contradicts that  $\beta$  is twice differentiable, an assumption that was used in the proof of Lemma 3.1, let us demonstrate that said lemma also applies in the



current setting with jump-discontinuous  $\beta$ :

$$\begin{aligned}
 & \lim_{m \rightarrow 0^+} \lim_{n \rightarrow \infty} m^{-1/2} \int_0^t \langle \bar{V}'' \cos\left(\frac{(t-s)\sqrt{\bar{V}''}}{\sqrt{m}}\right) \dot{a}(X_s), \partial_{X^\ell} a \rangle ds \\
 &= \sum_{\ell'} \lim_{m \rightarrow 0^+} m^{-1/2} \int_0^t \int_{\mathbb{R}^3} \cos\left(\frac{(t-s)\omega}{\sqrt{m}}\right) f(\omega, \ell, \ell') \frac{d\omega}{\omega^2} d\tau \dot{X}_s^{\ell'} ds \\
 &= \sum_{\ell'} \lim_{m \rightarrow 0^+} m^{-1/2} \int_0^t \int_0^1 \int_0^{2\pi} \int_0^\pi \cos\left(\frac{(t-s)\omega}{\sqrt{m}}\right) \sin(\theta) d\theta d\alpha d\omega \dot{X}_s^{\ell'} ds \\
 &= 4\pi \sum_{\ell'} \lim_{m \rightarrow 0^+} \int_0^t \frac{\sin((t-s)/\sqrt{m})}{(t-s)} \dot{X}_s^{\ell'} ds \\
 &= 4\pi \sum_{\ell'} \lim_{m \rightarrow 0^+} \int_0^{tm^{-1/2}} \frac{\sin(\tau)}{\tau} \dot{X}_{t-m^{1/2}\tau}^{\ell'} d\tau \\
 &= 2\pi^2 \sum_{\ell'} \dot{X}_t^{\ell'},
 \end{aligned}$$

where the last equality follows from  $\int_0^\infty \frac{\sin \tau}{\tau} d\tau = \pi/2$  and  $\dot{X}_t$  being continuous with respect to  $t$ . We conclude that

$$(63) \quad \kappa = 2\pi^2 \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} [1 \quad 1 \quad 1].$$

To prove the convergence (28), observe first that

$$K_\infty^{\ell\ell'}(\tau) = \int_{\mathbb{R}^3} \cos(\tau\omega) f(\omega) \frac{d\omega}{\omega^2} = 4\pi \frac{\sin(\tau)}{\tau}.$$

Introducing the mesh  $\tau_k = 2k\pi$  and

$$\dot{Y}_{t-\tau\sqrt{m}}^\ell := \sum_{k=0}^{\lfloor t/(\sqrt{m}2\pi) \rfloor} \mathbf{1}_{\tau \in [\tau_k, \tau_{k+1})} \dot{X}_{t-\tau_k\sqrt{m}}^\ell,$$

it follows that for any  $\tau \in [\tau_k, \tau_{k+1})$ , there exists a path-dependent  $s \in [\tau_k, \tau_{k+1})$  such that

$$|\dot{X}_{t-\tau\sqrt{m}}^\ell - \dot{Y}_{t-\tau\sqrt{m}}^\ell| = |\dot{X}_{t-s\sqrt{m}}^\ell| 2\pi\sqrt{m}.$$

By the splitting (30) with  $\tau_* = m^{-1/2} \min(t, 1)$ , we have

$$\begin{aligned}
& \left| \mathbb{E}[h(X_t, P_t) \int_0^{\tau_*} \sum_{\ell'} K_\infty^{\ell\ell'}(\tau) (\dot{X}_{t-\sqrt{m}\tau}^{\ell'} - \dot{X}_t^{\ell'}) d\tau] \right| \\
& \leq \left| \mathbb{E}[h(X_t, P_t) \int_0^{\tau_*} \sum_{\ell'} K_\infty^{\ell\ell'}(\tau) (\dot{X}_{t-\tau\sqrt{m}}^{\ell'} - \dot{Y}_{t-\tau\sqrt{m}}^{\ell'}) d\tau] \right| \\
& \quad + \left| \mathbb{E}[h(X_t, P_t) \int_0^{\tau_*} \sum_{\ell'} K_\infty^{\ell\ell'}(\tau) (\dot{Y}_{t-\tau\sqrt{m}}^{\ell'} - \dot{X}_t^{\ell'}) d\tau] \right| \\
& \leq C\sqrt{m} \sum_{k=0}^{\lfloor 1/(\sqrt{m}\pi) \rfloor} \int_{\tau_k}^{\tau_{k+1}} \frac{|\sin(\tau)|}{\tau} d\tau \\
& \leq C\sqrt{m} \sum_{k=1}^{\lfloor 1/(\sqrt{m}\pi) \rfloor} k^{-1} \\
& \leq C\sqrt{m} \max(1, \log(m^{-1})),
\end{aligned}$$

and, in the case  $t > 1$ ,

$$\begin{aligned}
& |\mathbb{E}[h(X_t, P_t) \int_{\tau_*}^{t/\sqrt{m}} \langle \bar{V}'' \cos(\tau \bar{V}''^{1/2}) \dot{a}(X_{t-\sqrt{m}\tau}), \partial_{X^\ell} a \rangle d\tau]| \\
& \leq |\mathbb{E}[h(X_t, P_t) \int_{1/\sqrt{m}}^{t/\sqrt{m}} \sum_{\ell'} K_\infty^{\ell\ell'}(\tau) (\dot{X}_{t-\tau\sqrt{m}}^{\ell'} - \dot{Y}_{t-\tau\sqrt{m}}^{\ell'}) d\tau]| \\
& \quad + |\mathbb{E}[h(X_t, P_t) \int_{1/\sqrt{m}}^{t/\sqrt{m}} \sum_{\ell'} K_\infty^{\ell\ell'}(\tau) \dot{Y}_{t-\tau\sqrt{m}}^{\ell'} d\tau]| \\
& \leq C \sum_{k=\lfloor 1/(\sqrt{m}\pi) \rfloor}^{\lfloor t/(\sqrt{m}\pi) \rfloor} \left( \sqrt{m} \int_{\tau_k}^{\tau_{k+1}} \frac{|\sin(\tau)|}{\tau} d\tau + \left| \int_{\tau_k}^{\tau_{k+1}} \frac{\sin(\tau)}{\tau} d\tau \right| \right) \\
& \leq C\sqrt{m} \max(1, \log(m^{-1})),
\end{aligned}$$

where  $\int_{\tau_k}^{\tau_{k+1}} \frac{\sin(\tau)}{\tau} d\tau = -\int_{2k\pi}^{2(k+1)\pi} \frac{\cos(\tau)}{\tau^2} d\tau$  to bound the last summand. For the current setting, equation (28) follows by the same reasoning as in the proof of Lemma 3.1.

**6.1. Dynamical systems.** For a given mass ratio  $m$ , the generalized Langevin equation of the heat bath dynamics takes the form

$$\begin{aligned}
\dot{X}(t) &= P(t) \\
\dot{P}(t) &= -\nabla\lambda(X(t)) - \int_0^t K_\infty\left(\frac{t-s}{\sqrt{m}}\right) P(s) ds + \zeta(t),
\end{aligned}$$

where  $\zeta(t)$  denotes a mean-zero Gaussian process with  $\zeta^1 = \zeta^2 = \zeta^3$  and

$$\mathbb{E}[\zeta^1(s)\zeta^1(t)] = TK_\infty^{11}((t-s)/\sqrt{m}),$$

cf. (35) and (36). The associated Langevin dynamics is

$$\begin{aligned}
\dot{X}_L(t) &= P_L(t) \\
\dot{P}_L(t) &= -\nabla\lambda(X_L(t)) - m^{1/2}\kappa P_L(t) + (2m^{1/2}\kappa T)^{1/2} \dot{W}(t)
\end{aligned}$$

with  $\kappa$  given by (63). We will compare the dynamical systems numerically for the initial data  $X_L(0) = X(0) = \xi_X(1, 1, 1)$  and  $P_L(0) = P(0) = \xi_P(1, 1, 1)$ , where  $\xi_X$  and  $\xi_P$  are independent identically distributed standard Gaussians that are sampled pathwise. Due to the initial data and  $\nabla\lambda(X) = X$ , it holds that  $X(t), P(t) \in \text{Span}((1, 1, 1))$  for all  $t \geq 0$ . For this particular example, it therefore suffices to study the reduced dynamics  $(X^1, P^1)$  and  $(X_L^1, P_L^1)$  rather than the respective 6 dimensional full systems. The respective reduced dynamics are equal in distribution to

$$\begin{aligned}\dot{X}^1(t) &= P^1(t) \\ \dot{P}^1(t) &= -X^1(t) - 12\pi\sqrt{m} \int_0^t \frac{\sin((t-s)/\sqrt{m})}{t-s} P^1(s) ds + \zeta^1(t),\end{aligned}$$

and

$$(64) \quad \begin{aligned}\dot{X}_L^1(t) &= P_L^1(t) \\ \dot{P}_L^1(t) &= -X_L^1(t) - 6\pi^2\sqrt{m}P_L^1(t) + 2\pi m^{1/4}T^{1/2}\dot{W}^1(t).\end{aligned}$$

**6.2. Numerical integration schemes.** Langevin dynamics (based on Störmer–Verlet/Ornstein–Uhlenbeck [21]):

$$\begin{aligned}P_{L,n+1/2}^* &= \exp(-6\pi^2\sqrt{m}\Delta t/2)P_{L,n}^1 + T^{1/2}\sqrt{\frac{1 - \exp(-12\pi^2\sqrt{m}\Delta t/2)}{3}}\xi_{2n-1} \\ P_{L,n+1/2}^1 &= P_{L,n+1/2}^* - X_{L,n}^1 \frac{\Delta t}{2} \\ X_{L,n+1}^1 &= X_{L,n}^1 + P_{L,n+1/2}^1 \Delta t \\ P_{L,n+1}^* &= P_{L,n+1/2}^1 - X_{L,n+1}^1 \frac{\Delta t}{2} \\ P_{L,n+1}^1 &= \exp(-6\pi^2\sqrt{m}\Delta t/2)P_{L,n+1}^* + T^{1/2}\sqrt{\frac{1 - \exp(-12\pi^2\sqrt{m}\Delta t/2)}{3}}\xi_{2n},\end{aligned}$$

where  $\xi_n$  is a sequence of independent and identically distributed standard normals. The scheme is motivated from the splitting method with symplectic integration of the Hamiltonian system

$$\dot{X}_L^1(t) = P_L^1(t), \quad \dot{P}_L^1(t) = -X_L^1(t)$$

and exact solution of the Ornstein–Uhlenbeck equation

$$\dot{P}_L^1(t) = -6\pi^2\sqrt{m}P_L^1(t) + 2\pi m^{1/4}T^{1/2}\dot{W}^1(t),$$

cf. [21].

For the heat bath dynamics we construct a splitting scheme which for a uniform mesh  $t_k = k\Delta t$  computes the position at every timestep  $(X^1(t_0), X^1(t_1), \dots)$  and the momentum at every half-timestep  $(P^1(t_0), P^1(t_{1/2}), P^1(t_1), \dots)$ . The damping

term's integral is approximated as follows:

$$\begin{aligned}
(65) \quad \int_0^{t_{n+1}} \frac{\sin((t_{n+1}-s)/\sqrt{m})}{t_{n+1}-s} P^1(s) ds &\approx \sum_{k=0}^n P^1(t_k) \int_{t_k}^{t_{k+1/2}} \frac{\sin((t_{n+1}-s)/\sqrt{m})}{t_{n+1}-s} ds \\
&\quad + \sum_{k=0}^n P^1(t_{k+1/2}) \int_{t_{k+1/2}}^{t_{k+1}} \frac{\sin((t_{n+1}-s)/\sqrt{m})}{t_{n+1}-s} ds \\
&= \sum_{k=0}^n \left[ P^1(t_k) (\text{Si}(t_{n+1-k}/\sqrt{m}) - \text{Si}(t_{n+1/2-k}/\sqrt{m})) \right. \\
&\quad \left. + P^1(t_{k+1/2}) (\text{Si}(t_{n+1/2-k}/\sqrt{m}) - \text{Si}(t_{n-k}/\sqrt{m})) \right],
\end{aligned}$$

where the last equality follows from

$$\int_a^b \frac{\sin((t_{n+1}-s)/\sqrt{m})}{t_{n+1}-s} ds = \int_{(t_{n+1}-b)/\sqrt{m}}^{(t_{n+1}-a)/\sqrt{m}} \frac{\sin(s)}{s} ds$$

and

$$\text{Si}(t) := \int_0^t \frac{\sin(s)}{s} ds.$$

Introducing the notation

$$\Delta \text{Si}_\ell := \text{Si}(t_{\ell+1/2}/\sqrt{m}) - \text{Si}(t_\ell/\sqrt{m}),$$

the approximation (65) takes the compact form

$$\int_0^{t_{n+1}} \frac{\sin((t_{n+1}-s)/\sqrt{m})}{t_{n+1}-s} P^1(s) ds \approx \sum_{k=0}^n P^1(t_k) \Delta \text{Si}_{n+1/2-k} + P^1(t_{k+1/2}) \Delta \text{Si}_{n-k},$$

and, similarly,

$$\begin{aligned}
\int_0^{t_{n+1/2}} \frac{\sin((t_{n+1/2}-s)/\sqrt{m})}{t_{n+1/2}-s} P^1(s) ds &\approx \sum_{k=0}^n P^1(t_k) \Delta \text{Si}_{n-k} \\
&\quad + \sum_{k=0}^{n-1} P^1(t_{k+1/2}) \Delta \text{Si}_{n+1/2-k}.
\end{aligned}$$

We make use of the above approximations of the damping term integral in the following splitting scheme for the heat bath dynamics:

$$\begin{aligned}
P_{n+1/2}^1 &= P_n^1 - \frac{\Delta t}{2} \left[ X_n^1 - \zeta^1(t_n) \right. \\
&\quad \left. + 12\pi\sqrt{m} \left( \sum_{k=0}^n P_k^1 \Delta \text{Si}_{n-k} + \sum_{k=0}^{n-1} P_{k+1/2}^1 \Delta \text{Si}_{n+1/2-k} \right) \right] \\
X_{n+1}^1 &= X_n^1 + P_{n+1/2}^1 \Delta t \\
P_{n+1}^1 &= P_{n+1/2}^1 - \frac{\Delta t}{2} \left[ X_{n+1}^1 - \zeta^1(t_{n+1}) \right. \\
&\quad \left. + 12\pi\sqrt{m} \sum_{k=0}^n P_k^1 \Delta \text{Si}_{n+1/2-k} + P_{k+1/2}^1 \Delta \text{Si}_{n-k} \right].
\end{aligned}$$

The mean-zero Gaussian vector  $\zeta = (\zeta^1(t_0), \zeta^1(t_1), \dots, \zeta^1(t_N))$  is sampled by computing the square root of the Toeplitz matrix with first row vector

$$(TK_\infty(0^+/\sqrt{m}), TK_\infty(t_1/\sqrt{m}), \dots, TK_\infty(t_N/\sqrt{m}))$$

and multiplying the square root matrix, say  $\sqrt{K}$ , with an  $(N+1)$ -vector  $\xi$  of iid standard normals components:  $\zeta = \sqrt{K}\xi$ . See [11] for further details on sampling of Gaussian processes, [5, 24, 16, 19, 3, 1, 17] for numerical methods for Langevin dynamics and [2, 9, 13] and [16, Chapter 8.7] for an alternative numerical method for generalized Langevin equations based on a truncated Prony series approximation of the kernel  $K_\infty$ .

**6.3. Observations.** By setting the temperature to  $T = 3$ , the stationary distribution of the exact Langevin dynamics (64) becomes  $N(0, I)$  for any  $m > 0$ , with  $I$  denoting the identity matrix in  $\mathbb{R}^2$ . In order to reduce the computational challenges of long time numerical integration, we sample the initial data from this stationary, i.e.,  $(\xi_X, \xi_P) \sim N(0, I)$ , as we assume this yields initial data for the numerical dynamics  $(X_{L,0}^1, P_{L,0}^1)$  and  $(X_0^1, P_0^1)$  that are very close to their respective stationary distributions. The numerical computations are performed using  $\Delta t = 0.005$ ,  $N = 4000$  integration steps relating to the final time  $t_N = 20$ , and  $M = 2 \times 10^5$  solution realizations of the respective dynamics. Figure 1 shows good correspon-

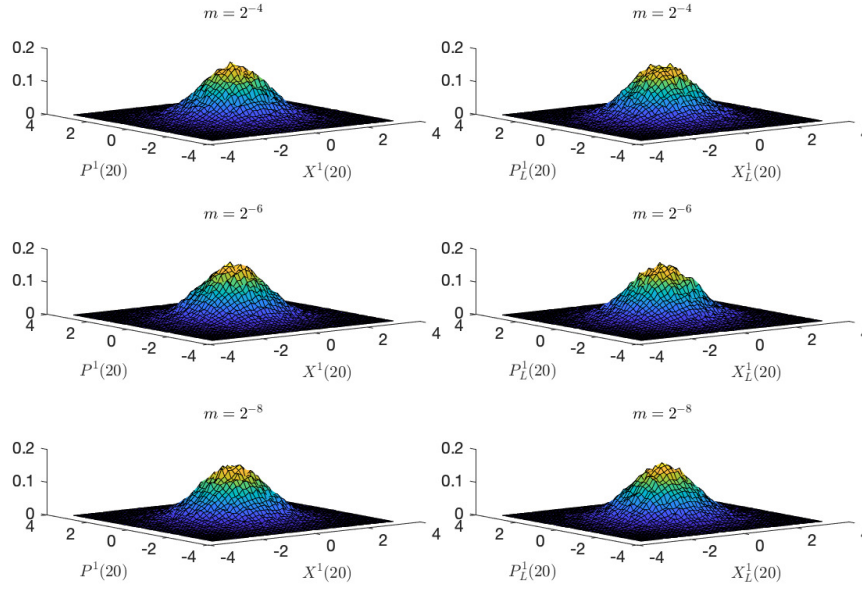


FIGURE 1. (Left column) unit-volume scaled histogram for the final time position and momentum of the heat bath dynamics for a series of  $m$ -values and (right column) corresponding histograms for the Langevin dynamics.

dence between the final time joint distribution of the heat bath dynamics  $(X_N^1, P_N^1)$

and the Langevin dynamics  $(X_{L,N}^1, P_{L,N}^1)$  over a range of  $m$ -values (all being approximately  $N(0, I)$ -distributed). Figures 2 and 3 show that the autocorrelation for both the position and the momentum of the heat bath dynamics converges to the corresponding ones for the Langevin dynamics as  $m \rightarrow 0^+$ . The computa-

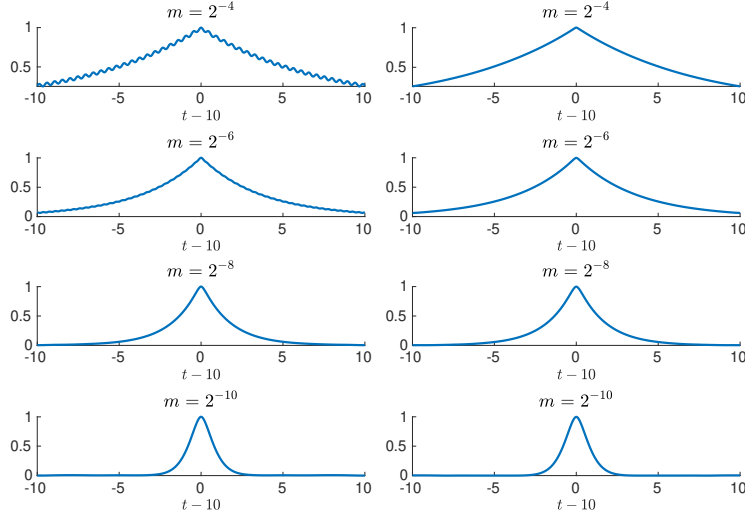


FIGURE 2. (Left column) heat bath dynamics autocorrelation function  $\mathbb{E}[X^1(t)X^1(10)]$  for a series of  $m$ -values and (right column) corresponding Langevin dynamics autocorrelation functions  $\mathbb{E}[X_L^1(t)X_L^1(10)]$ .

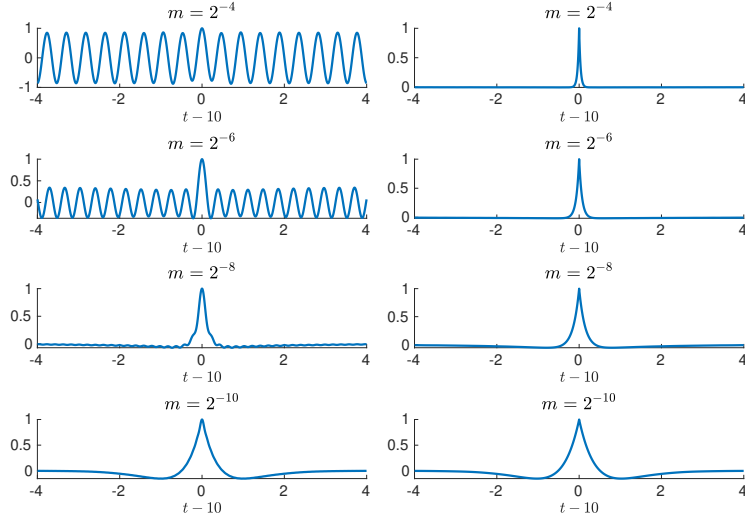


FIGURE 3. (Left column) heat bath dynamics autocorrelation function  $\mathbb{E}[P^1(t)P^1(10)]$  for a series of  $m$ -values and (right column) corresponding Langevin dynamics autocorrelation functions  $\mathbb{E}[P_L^1(t)P_L^1(10)]$ .

tions of the autocorrelation functions are made under the assumption that both kinds of dynamics are wide-sense stationary. For any  $m > 0$  this property holds for the Langevin dynamics, and in the limit  $m \rightarrow 0^+$  it also holds for the heat bath dynamics.

In addition to our above observations, we believe it would be of great interest to obtain numerical verification for the heat bath dynamics weak convergence rate  $\mathcal{O}(m^{1/2})$  in (45). But, most likely due to computational constraints, we are unable to achieve this currently since even at the quite computationally demanding level of generating  $M = 200000$  heat bath dynamics sample paths, it seems that the sample error dominates errors pertaining to the parameter  $m$ .

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*E-mail address:* `hoel@uq.rwth-aachen.de`

*E-mail address:* `szepessy@kth.se`