Fokker-Planck equation for lattice vibration: Stochastic dynamics and thermal conductivity

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We propose a Fokker-Planck equation (FPE) theory to describe stochastic fluctuation and relaxation processes of lattice vibration at a wide range of conditions, including those beyond the phonon gas limit. Using the time-dependent, multiple state-variable probability function of a vibration FPE, we first derive time-correlation functions of lattice heat currents in terms of correlation functions among multiple vibrational modes, and subsequently predict the lattice thermal conductivity based on the Green-Kubo formalism. When the quasiparticle kinetic transport theories are valid, this vibration FPE not only predicts a lattice thermal conductivity that is identical to the one predicted by the phonon Boltzmann transport equation, but also provides additional microscopic details on the multiple-mode correlation functions. More importantly, when the kinetic theories become insufficient due to the breakdown of the phonon gas approximation, this FPE theory remains valid to study the correlation functions among vibrational modes in highly anharmonic lattices with significant mode-mode interactions and/or in disordered lattices with strongly localized modes. At the limit of weak mode-mode interactions, we can adopt quantum perturbation theories to derive the drift/diffusion coefficients based on the lattice anharmonicity data derived from first-principles methods. As temperature elevates to the classical regime, we can perform molecular dynamics simulations to directly compute the drift/diffusion coefficients. Because these coefficients are defined as ensemble averages at the limit of $\delta t \to 0$, we can implement massive parallel simulation algorithms to take full advantage of the paralleled high-performance computing platforms. A better understanding of the temperature-dependent drift/diffusion coefficients up to melting temperatures will provide new insights on microscopic mechanisms that govern the heat conduction through anharmonic and/or disordered lattices beyond the phonon gas model.

I. INTRODUCTION

The phonon Boltzmann transport equation (BTE) [1,2] has gained some renewed interests as the default choice of transport theory to compute lattice thermal conductivity (κ_{Latt}) of crystalline solids from first principles [3–9]. The theoretical foundation of the phonon BTE is the so-called phonon gas (PG) model [10–13], which assumes that interactions among vibrational modes are weak enough that the numbers of phonons of each mode follow the single-particle Bose-Einstein distribution at equilibrium. As a kinetic theory, the phonon BTE further assumes that (1) each quasiparticle phonon travels at a group velocity $\vec{v}_g$, and (2) the lifetime τ of every phonon is finite because of the scatterings by lattice anharmonicity, lattice defects/disorder, or other particles. For electronic insulators, the necessary inputs for a phonon BTE calculation are the harmonic phonon spectra and the phonon-scattering terms, both of which can be numerically calculated using first-principles methods [4,14–22]. Multiple implementations of the phonon BTE methods have been reported in recent years [23–27], and the calculated results adopting various theoretical and numerical approximations have been

systematically bench-marked among themselves and compared with available experimental data. The overall good agreement between the first-principles computational results and available experimental data for a large amount of crystals at moderate temperatures (T) establishes the phonon BTE as a practical and robust computational tool to design advanced technology materials with optimized thermal transport properties.

Meanwhile, concerns have been raised about the validity of the phonon BTE beyond the PG limit, where interactions among vibrational modes are significant and the weakly interacting quasiparticle approximation becomes insufficient [28]. A schematic plot of a typical temperature dependence of κ_{Latt} in crystals is shown in Fig. 1. Within the PG approximation, the phonon BTE predicts that κ_{Latt} of a crystal decays to zero with increasing T at the rate of $1/T$ or faster. However, experimental measurements [29,30] reveal that the deviation from the $1/T$ scaling become noticeable as T approaches the melting temperature (T_{melt}) of the lattice, with κ_{Latt} eventually reaching a low constant value. The omnipresence of these minimal thermal conductivities (κ_{min}) [31] in all crystalline lattices suggests that as a lattice approaches its T_{melt}, the increasingly strong anharmonic coupling among vibrational modes causes the breakdown of the PG model. Such breakdown might occur at moderate

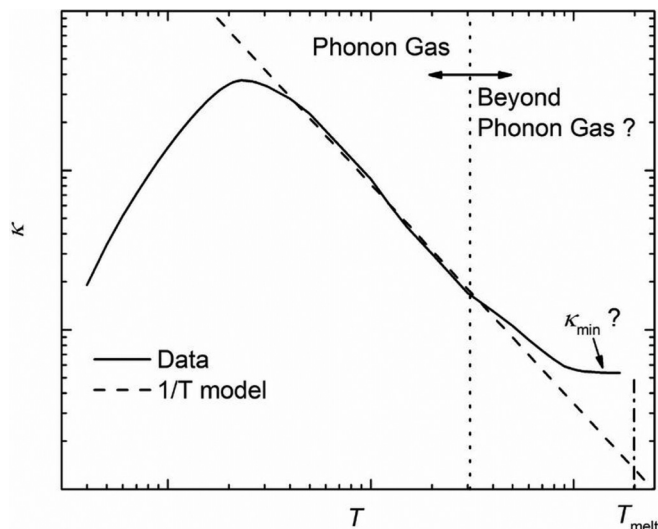*Corresponding author: dongjia@auburn.edu

FIG. 1. Schematic plot of lattice thermal conductivity κ_{Latt} as a function of temperature T, up to the melting temperature T_{melt}.

temperatures in relatively soft solids with large thermal expansion [32–34] or in the high temperature phases of solids whose 0 K phonon spectra contain imaginary frequencies [35]. In addition, the phonon BTE incorporates the concept of phonon group velocity, which is not properly defined in nonperiodic solids such as alloys, glass, or amorphous semiconductors [36], even at the conditions where all the vibrational modes remain quasiharmonic [37].

When the accuracy of the phonon BTE theory is in question, the statistical linear response transport theory [38] is often combined with equilibrium molecular dynamics (MD) simulations to predict thermal transport properties [39–42]. For example, the Green-Kubo (GK) formalism states that thermal conductivity is proportional to the time-integral of the auto-correlation function of heat flux [43,44]. Although the GK method is theoretically rigorous and valid beyond the PG approximation, its current implementations, based on the evaluations of atomic trajectories, i.e., displacements and velocities, over a long period of time, usually require much more intensive computational loads. When no reliable empirical force-field interatomic potentials exist, *ab initio* MD simulations are necessary to simulate the complex lattice vibration. Yet, in practice, typical *ab initio* MD simulations are often carried out with only relatively short simulation periods (i.e., on the order of a few picoseconds) and using relatively small supercell models (i.e., on the order of a couple of hundred atoms) because their computational loads scale as order N^3, where N is the number of atoms in a supercell model. These numerical finite-size artifacts sometimes impose relatively large uncertainties in the *ab initio* MD simulation results. Additional approximations are often needed to extract potential energy of each atom from the *ab initio* total energies of the supercell models to evaluate the correlation function of heat currents using the *ab initio* MD simulation results [45–49].

More importantly, all the atomic trajectories in MD simulations have to be calculated numerically, even at the weak scattering limit of the PG model. This lack of analytical solutions of atomic trajectories in MD simulations hinders the development of quantitative theoretical models to interpret

the simulated current-current correlation functions because it provides little insight on improving/correcting the PG model beyond the weak scattering limit. Ladd *et al.* [50] proposed a normal mode analysis (NMA) approach to evaluate the phonon lifetimes τ based on the damped oscillator approximation (DOA). Using the extracted phonon lifetimes, they derived the so-called Peierls phonon-transport expression of κ_{Latt}, which is understood to be only an approximate solution of the phonon BTE theory. Nevertheless, these types of NMA methods have been useful to interpret the phonon scattering in a MD simulation, and these methods have been implemented and further developed in recent years by many groups using both empirical potentials and *ab initio* methods [51–54]. However, both the DOA and the concept of phonon lifetime/relaxation-time should be adopted only as semiquantitative models because the cross-correlations among different vibrational modes can not always be neglected. More robust theoretical models or concepts are needed to quantitatively interpret the NMA results of numerical MD simulations.

In this paper, we present a time-dependent statistical theory to quantitatively describe the thermal fluctuation and correlation properties of vibrational modes using a Fokker-Planck equation [55] for lattice dynamics. First, this vibration FPE theory does not treat the interactions among different vibrational modes as small perturbations. Instead, our theory includes two general sets of parameters, the drift A and the diffusion B coefficients, to explicitly characterize the mode-mode interactions. The results of this vibration FPE, expressed in terms of a time-dependent probability function of multiple-variable vibrational microstates, provide details of the dynamic relaxation processes of lattice vibration, and are readily used by the linear response transport theory to compute κ_{Latt} beyond the quasiharmonic PG model.

Second, this vibration FPE provides detailed information on the time-correlation properties of physical quantities without requirement of long-time MD simulations. The proposed vibration FPE derives the correlation functions based on the probability function governed by the drift A and diffusion B coefficients, which are defined in terms of ensemble averages at the $\delta t \to 0$ limit. It is important to emphasize that no *a priori* forms of correlation functions are assumed in a FPE calculation of correlation functions. As a result, when implemented with first-principles methods, this vibration FPE is promising to be both accurate and efficient to predict κ_{Latt} of novel and complex solids at wide-ranging conditions.

Finally, the κ_{latt} predicted by the vibration FPE converges to the one from the conventional phonon BTE within the PG model. Because the FPE's parameters of a lattice vibration can be evaluated with either perturbative methods or simulation methods at the PG approximation, our vibration FPE theory establishes a systematical computational methodology to analyze errors of the simple PG model and to delineate the breakdown conditions of the PG approximation.

II. STOCHASTIC DYNAMICS OF LATTICE VIBRATION

A. Fokker-Planck equation

The first fundamental assumption of this proposed Fokker-Planck equation for lattice vibration is that thermal lattice

dynamics is a stochastic process at the microscopic level, and the probabilistic transition dynamics from one vibration microstate Γ to other thermally accessible microstates can be modeled with a statistical master equation [38,55]. When a specific microstate Γ^0 is sampled at time $t = 0$, the initial probability function is simply

$$P(\Gamma, t = 0|\Gamma^0) = \delta(\Gamma - \Gamma^0). \tag{1}$$

Regardless of the dynamic details of a stochastic process, the equilibrium ensemble theory constrains that at the long-time limit of $t \to \infty$, the probability function evolves into the canonical distribution function:

$$P(\Gamma, t \to \infty|\Gamma^0) \to P_{eq}(\Gamma) = \frac{e^{\frac{-E(\Gamma)}{k_B T}}}{Z_{eq}(T)}, \tag{2}$$

where k_B is the Boltzmann constant, T represents temperature, $E(\Gamma)$ denotes the energy of any microstate Γ, and $Z_{eq}(T)$ denotes the equilibrium canonical partition function of the lattice vibration. The evolution of this probability function $P(\Gamma, t|\Gamma^0)$ provides a general and quantitative description of lattice thermal relaxation processes, from a single initially sampled microstate Γ^0 to a set of the thermally accessible microstates that correspond to an equilibrium distribution governed by the equilibrium statistics. Here, the ergodic condition in lattice vibration is assumed.

We further adopt the Born-von-Karman periodic boundary condition [10] to specify the vibrational microstates with total N vibration modes, with $N \to \infty$ for an infinitely large crystal. When the αth vibrational mode is occupied by n_α phonons, the vibrational mode is thermally excited to the quantum number n_α, which is often referred as the number of phonons at the αth mode. We can further specify a vibrational micro-state with a set of N-dimensional state-variables $\Gamma = \{n_1, n_2, \cdots, n_N\}$ that represent the number of phonons at each of the N vibrational modes. Through the Kramers-Moyal expansion of the master equation, the time-evolution of this probability function $P(\Gamma, t|\Gamma^0) = P(n_1, n_2, \cdots, n_N, t|n_1^0, n_2^0, \cdots, n_N^0)$ can be expressed in the form of a FPE [38,55]:

$$\frac{\partial P}{\partial t} = -\sum_{\alpha=1}^{N} \frac{\partial}{\partial n_\alpha}[A_\alpha(\Gamma) \cdot P] + \frac{1}{2}\sum_{\alpha\beta} \frac{\partial^2}{\partial n_\alpha \partial n_\beta}[B_{\alpha\beta}(\Gamma) \cdot P]. \tag{3}$$

The assumption of a FPE is that the third-order expansion coefficients are approximately zero. According to the Pawula theorem, all the higher order expansion coefficients are zero if the third-order expansion coefficients are zero [55]. Within this theoretical framework, the drift $A_\alpha(\Gamma)$ and diffusion $B_{\alpha\beta}(\Gamma)$ coefficients manifest the interactions among vibrational modes, and they are defined as

$$A_\alpha(\Gamma) \equiv \lim_{\delta t \to 0} \frac{1}{\delta t} \int_0^{\delta t} d\Gamma' \delta n_\alpha(\Gamma, \Gamma') P(\Gamma', \delta t|\Gamma),$$

$$B_{\alpha\beta}(\Gamma) \equiv \lim_{\delta t \to 0} \frac{1}{\delta t} \int_0^{\delta t} d\Gamma' \delta n_\alpha(\Gamma, \Gamma') \delta n_\beta(\Gamma, \Gamma') P(\Gamma', \delta t|\Gamma). \tag{4}$$

In the case that a stochastic lattice vibration can be modeled as a random process of transition from one vibrational microstate Γ to another microstate Γ' with a known rate of transition $w_{\Gamma \to \Gamma'}$, Eqs. (4) can be approximated as

$$A_\alpha(\Gamma) \approx \int d\Gamma'[n_\alpha(\Gamma') - n_\alpha(\Gamma)] \cdot w_{\Gamma \to \Gamma'},$$

$$B_{\alpha\beta}(\Gamma) \approx \int d\Gamma'[n_\alpha(\Gamma') - n_\alpha(\Gamma)]$$
$$\cdot [n_\beta(\Gamma') - n_\beta(\Gamma)] \cdot w_{\Gamma \to \Gamma'}. \tag{5}$$

Within this statistical probability theory [Eq. (3)], the dynamic details of a stochastic lattice vibration rely on the knowledge of both drift A and diffusion B coefficients. As formulated in Eqs. (4), both A and B coefficients can be numerically calculated based on an ensemble of microscopic simulations over a short period of simulation time δt. Because of the short simulation periods for the parameter evaluation, it becomes practical to implement the numerical simulations using accurate first-principles methods. The overall computational loads of ensemble averages, although still intensive, can be, in principle, distributed over a cluster of computer nodes to take full advantage of the state-of-the-art parallel high-performance computing platforms. Choosing an appropriate simulation period δt for the parameter calculations is not merely a numeric issue. The length of δt reflects the level of temporal coarse-graining. For example, in a bulk system, δt should be larger than the oscillating periods, as well as the ballistic time periods, to ensure the assumption of a thermal relaxation process. In addition, different values δt might be needed when there are more than one drift/diffusion mechanism. In an amorphous lattice, the drift/diffusion timescale for an extended vibrational mode likely differs significantly from that of a strongly localized vibration mode. Extensive future studies are needed to gain a better understanding these coefficients of a vibration FPE.

On one hand, the general forms for the A and B coefficients defined in Eqs. (4) imply that our proposed vibration FPE theory does not limit the magnitude of the mode-mode interactions in a lattice to be perturbatively small, nor does it require each mode correspond to a traveling wave with a specific group velocity $\vec{v}_\alpha$. Consequently, this vibration FPE, as formulated in Eq. (3), is valid for lattice vibration with a broad range of mode-mode interactions, including lattice vibration with strong anharmonic modes and/or disorder-induced spatially localized modes. On the other hand, in the weak scattering case that both initial (Γ) and final (Γ') quantum vibration states can be represented by the phonon representation $|n_1, n_2, n_3, \cdots, n_N >$, and $\Delta \hat{V}$ denotes perturbatively small deviations in the vibration Hamiltonian from that of the ideal PG, we can simply adopt Eqs. (5) to evaluate the A and B coefficients based on the rates of transition derived from the Fermi's golden rule:

$$w_{\Gamma \to \Gamma'} = \frac{2\pi}{\hbar} |\langle n_1', n_2', n_3', \cdots,$$
$$n_N'|\Delta \hat{V}|n_1, n_2, n_3, \cdots, n_N \rangle|^2. \tag{6}$$

B. Thermal relaxation: Fluctuation and correlation

At thermal equilibrium, the instantaneous value of a quantity X, either macroscopic or microscopic, fluctuates around its equilibrium value X_{eq}. The dynamical process that brings the fluctuating value of $X(t)$ back toward the X_{eq} is commonly referred as a thermal relaxation process. A self-correlation function of X,

$$C_{XX}(t) \equiv \langle \delta X(0) \cdot \delta X(t) \rangle_{eq} = \langle (X(0) - X_{eq}) \cdot (X(t) - X_{eq}) \rangle_{eq}, \tag{7}$$

is often used to quantify the properties of this thermal relaxation process. When X can be expressed in terms of microstate variables $X(\Gamma)$, we can define a time-dependent expectation value $\overline{X}(t|\Gamma^0)$ based on the probability function $P(\Gamma, t|\Gamma^0)$ in the vibration FPE, staring with the initial probability function shown in Eq. (1):

$$\overline{X}(t|\Gamma^0) \equiv \int d\Gamma P(\Gamma, t|\Gamma^0) \cdot X(\Gamma),$$

$$\frac{d\overline{X}(t|\Gamma^0)}{dt} \equiv \int d\Gamma \frac{\partial P(\Gamma, t|\Gamma^0)}{\partial t} \cdot X(\Gamma)$$

$$= \sum_\alpha \overline{\left[\frac{\partial X}{\partial n_\alpha} \cdot A_\alpha \right]}(t|\Gamma^0) + \frac{1}{2} \sum_{\alpha\beta} \overline{\left[\frac{\partial^2 X}{\partial n_\alpha \partial n_\beta} \cdot B_{\alpha\beta} \right]}(t|\Gamma^0). \tag{8}$$

Clearly, $\overline{X}(t)$ starts at its initial value of $X(\Gamma^0) = \int d\Gamma \delta(\Gamma - \Gamma^0) X(\Gamma)$, and eventually relaxes back to its equilibrium value of $X_{eq} = \int d\Gamma X(\Gamma) P_{eq}(\Gamma)$ when $P(\Gamma, t|\Gamma^0) \to P_{eq}(\Gamma)$ at the limit of $t \to \infty$. Similarly, the corresponding time-dependent statistical variance, defined as $\Delta_X(t|\Gamma_0) \equiv \overline{X^2}(t|\Gamma_0) - \overline{X}(t|\Gamma_0)^2$, relaxes from its initial value of 0 to its equilibrium value $\Delta_{X,eq} = \int d\Gamma (X(\Gamma) - X_{eq})^2 \cdot P_{eq}(\Gamma) > 0$.

By sampling the initial microstates Γ^0 with the equilibrium probability function $P_{eq}(\Gamma^0)$, we can rewrite the time-correlation function of X, defined in Eq. (7), as

$$C_{XX}(t) = \langle \delta X(\Gamma_0) \cdot \overline{\delta X}(t|\Gamma_0) \rangle_{eq}$$

$$= \int d\Gamma_0 P_{eq}(\Gamma_0)(X(\Gamma_0) - X_{eq}) \int d\Gamma P(\Gamma, t|\Gamma_0)(X(\Gamma) - X_{eq}), \tag{9}$$

where $C_{XX}(t = 0) = \Delta_{X,eq}$, and $C_{XX}(t \to \infty) \to [\int d\Gamma_0(X(\Gamma_0) - X_{eq}) \cdot P_{eq}(\Gamma_0)] \cdot [\int d\Gamma P_{eq}(\Gamma) \cdot (X(\Gamma) - X_{eq})] = 0$. A concept of an effective relaxation time (τ_X) of X is frequently adopted as the time integration of the normalized self-correlation function $c_{XX}(t) \equiv C_{XX}(t)/\Delta_{X,eq}$:

$$\tau_X \equiv \int_0^\infty c_{XX}(t) dt, \tag{10}$$

based on the approximation that $c_{XX}(t) \approx e^{-t/\tau_X}$.

The dynamical correlation between two different quantities X and Y that fluctuate around their prospective equilibrium values (X_{eq} and Y_{eq} can be quantitatively formulated in terms of a cross-correlation function $C_{XY}(t)$:

$$C_{XY}(t) \equiv \langle \delta X(0) \cdot \delta Y(t) \rangle_{eq} = \langle (X(0) - X_{eq}) \cdot (Y(t) - Y_{eq}) \rangle_{eq}, \tag{11}$$

and this cross-correlation function can be rewritten using the probability distribution function $P(\Gamma, t|\Gamma_0)$ of Eq. (3):

$$C_{XY}(t) = \langle \delta X(\Gamma_0) \cdot \overline{\delta Y}(t|\Gamma_0) \rangle_{eq}$$

$$= \int d\Gamma_0 P_{eq}(\Gamma_0)(X(\Gamma_0) - X_{eq}) \int d\Gamma P(\Gamma, t|\Gamma_0)(Y(\Gamma) - Y_{eq}), \tag{12}$$

where $C_{XY}(t \to \infty) \to [\int d\Gamma_0(X(\Gamma_0) - X_{eq}) \cdot P_{eq}(\Gamma_0)] \cdot [\int d\Gamma P_{eq}(\Gamma) \cdot (Y(\Gamma) - Y_{eq})] = 0$. Since $C_{XY}(t = 0) = \int d\Gamma_0 P_{eq}(\Gamma_0)(X(\Gamma_0) - X_{eq}) \cdot (Y(\Gamma_o) - Y_{eq}) = \langle (X - X_{eq}) \cdot (Y - Y_{eq}) \rangle_{eq}$, the ratio $c_{XY} \equiv C_{XY}(t = 0)/\sqrt{\Delta_{X,eq} \cdot \Delta_{Y,eq}}$ is often referred as the correlation ratio, with $c_{XY} = 0$ being interpreted as that the fluctuations in X and Y are statistically uncorrelated at thermal equilibrium. It is important to emphasize that even at the condition of uncorrelated fluctuation at $t = 0$, i.e., $C_{XY}(t = 0) = 0$, a time-dependent cross-correlation function defined in Eq. (12) is not always zero at $t > 0$. An example is shown in Eq. (28) of Sec. II C.

Because the self-correlation function formula in Eq. (9) is a special case of the cross-correlation function formula in Eq. (12) with $X = Y$, we present only the results of the time derivative of the cross-correlation function here based on Eqs. (8) and (12):

$$\frac{dC_{XY}(t)}{dt} = \int d\Gamma_0 P_{eq}(\Gamma_0) \delta X(\Gamma_0) \frac{d\overline{\delta Y}(t|\Gamma_0)}{dt}$$

$$= \int d\Gamma_0 P_{eq}(\Gamma_0) \delta X(\Gamma_0) \cdot \left\{ \sum_\mu \overline{\left[\frac{\partial Y}{\partial n_\mu} \cdot A_\mu \right]}(t|\Gamma^0) + \frac{1}{2} \sum_{\mu\nu} \overline{\left[\frac{\partial^2 Y}{\partial n_\mu \partial n_\nu} \cdot B_{\mu\nu} \right]}(t|\Gamma^0) \right\}. \tag{13}$$

where A and B are the parameters [Eqs. (4)] of the vibration FPE [Eq. (3)]. Using the definitions of $y_\mu \equiv \frac{\partial Y}{\partial n_\mu} \cdot A_\mu$ and $y_{\mu\nu} \equiv \frac{\partial^2 Y}{\partial n_\mu \partial n_\nu} \cdot B_{\mu\nu}$, we can rewrite Eq. (13) in terms of the cross-correlation functions between X and y_μ and those between X and $y_{\mu\nu}$:

$$
\begin{aligned}
\frac{dC_{XY}(t)}{dt} &= \sum_\mu \langle \delta X(0) \cdot y_\mu(t) \rangle_{\rm eq} + \frac{1}{2} \sum_{\mu\nu} \langle \delta X(0) \cdot y_{\mu\nu}(t) \rangle_{\rm eq} \\
&= \sum_\mu \langle \delta X(0) \cdot \delta y_\mu(t) \rangle_{\rm eq} + \frac{1}{2} \sum_{\mu\nu} \langle \delta X(0) \cdot \delta y_{\mu\nu}(t) \rangle_{\rm eq} \\
&= \sum_\mu C_{Xy_\mu}(t) + \frac{1}{2} \sum_{\mu\nu} C_{Xy_{\mu\nu}}(t).
\end{aligned}
\tag{14}
$$

Furthermore, all the higher order time derivatives of $C_{XY}(t)$ functions can also be derived from Eq. (14) in a recursive fashion.

Next, we summarize some key results in the case that X and Y are simply the αth and βth state variables n_α and n_β, with more details on the mathematical derivation given in Appendix A. The commonly adopted concept of phonon occupation number of a vibrational mode can be generalized as the time-dependent expectation value of the state variable n_α during a thermal relaxation process, i.e., $\overline{n}_\alpha(t|\Gamma^0) \equiv \int d\Gamma \, n_\alpha P(\Gamma, t|\Gamma^0)$, with $\overline{n}_\alpha(t|\Gamma^0) \to n_{\alpha,\rm eq}$ and $\Delta_\alpha(t|\Gamma^0) \equiv \overline{n_\alpha^2}(t|\Gamma^0) - \overline{n}_\alpha(t|\Gamma^0)^2 \to \Delta_{\alpha,\rm eq}$ at the $t \to \infty$ limit. At the weak phonon-scattering limit of the PG model, the thermal equilibrium values of $n_{\alpha,\rm eq}$ follow the Bose-Einstein distribution, and the corresponding statistical variances are $\Delta_{\alpha,\rm eq} = n_{\alpha,\rm eq}(n_{\alpha,\rm eq} + 1)$. Applying the vibration FPE [Eq. (3) to Eq. (8)], we derive the time derivatives of $\overline{n}_\alpha(t|\Gamma^0)$ and $\Delta_\alpha(t|\Gamma^0)$ as

$$
\begin{aligned}
\frac{d}{dt} \overline{n}_\alpha(t|\Gamma^0) &= \int d\Gamma \, A_\alpha(\Gamma) P(\Gamma, t|\Gamma^0) = \overline{A_\alpha}(t|\Gamma^0), \\
\frac{d}{dt} \Delta_\alpha(t|\Gamma^0) &= \overline{B_{\alpha\alpha}}(t|\Gamma^0) + 2 \cdot [\overline{n_\alpha A_\alpha}(t|\Gamma^0) - \overline{n}_\alpha(t|\Gamma^0) \cdot \overline{A_\alpha}(t|\Gamma^0)].
\end{aligned}
\tag{15}
$$

Furthermore, using Eqs. (11) and (12), we define the cross-correlation functions between the fluctuating phonon numbers of the αth mode and the βth mode (also referred to as two-mode correlation functions) as $C_{n_\alpha n_\beta}(t) \equiv \langle \delta n_\alpha(0) \cdot \delta n_\beta(t) \rangle_{\rm eq} = \langle n_\alpha(0) \cdot n_\beta(t) \rangle_{\rm eq} - n_{\alpha,\rm eq} \cdot n_{\beta,\rm eq}$, with $C_{n_\alpha n_\beta}(t=0) = \langle \delta n_\alpha \cdot \delta n_\beta \rangle_{\rm eq} = \langle n_\alpha \cdot n_\beta \rangle_{\rm eq} - n_{\alpha,\rm eq} \cdot n_{\beta,\rm eq}$. We can further define the normalized two-mode correlation functions as

$$
c_{\alpha\beta}(t) \equiv \frac{C_{n_\alpha n_\beta}(t)}{\sqrt{\Delta_{\alpha,\rm eq} \cdot \Delta_{\beta,\rm eq}}} = \frac{\int d\Gamma^0 P_{\rm eq}(\Gamma^0) \delta n_\alpha(\Gamma^0) \cdot \overline{\delta n_\beta}(t|\Gamma^0)}{\sqrt{\Delta_{\alpha,\rm eq} \cdot \Delta_{\beta,\rm eq}}}.
\tag{16}
$$

Since $X = n_\alpha$ and $Y = n_\beta$, we have $y_\mu = A_\beta \cdot \delta_{\mu\beta}$ and $y_{\mu\nu} = 0$. Using Eq. (14), we can show that

$$
\frac{dc_{\alpha\beta}(t)}{dt} = \frac{C_{n_\alpha A_\beta}(t)}{\sqrt{\Delta_{\alpha,\rm eq} \cdot \Delta_{\beta,\rm eq}}} = \frac{\langle \delta n_\alpha(0) A_\beta(t) \rangle_{\rm eq}}{\sqrt{\Delta_{\alpha,\rm eq} \cdot \Delta_{\beta,\rm eq}}} = \frac{\int d\Gamma^0 P_{\rm eq}(\Gamma^0) \delta n_\alpha(\Gamma^0) \cdot \overline{A_\beta}(t|\Gamma^0)}{\sqrt{\Delta_{\alpha,\rm eq} \cdot \Delta_{\beta,\rm eq}}}.
\tag{17}
$$

Multiple-mode correlation functions can be defined in a similar fashion. For example, there is only one type of three-mode correlation function among the αth, βth, and γth modes:

$$
\begin{aligned}
\langle \delta n_\alpha(0) \cdot \delta n_\beta(0) \cdot \delta n_\gamma(t) \rangle_{\rm eq} &= \int d\Gamma^0 P_{\rm eq}(\Gamma^0) \delta n_\alpha(\Gamma^0) \cdot \delta n_\beta(\Gamma^0) \cdot \overline{\delta n_\gamma}(t|\Gamma^0) \\
&= \int d\Gamma^0 P_{\rm eq}(\Gamma^0)(n_\alpha(\Gamma^0) - n_{\alpha,eq}) \cdot (n_\beta(\Gamma^0) - n_{\beta,\rm eq}) \int d\Gamma \, P(\Gamma, t|\Gamma^0)(n_\gamma(\Gamma) - n_{\gamma,\rm eq}),
\end{aligned}
\tag{18}
$$

and there are three types of four-mode correlation functions among four (α, β, μ, and ν) modes:

$$
\begin{aligned}
&\langle \delta n_\alpha(0) \delta n_\beta(0) \delta n_\mu(0) \delta n_\nu(t) \rangle_{\rm eq} \\
&= \int d\Gamma^0 P_{\rm eq}(\Gamma^0) \delta n_\alpha(\Gamma^0) \cdot \delta n_\beta(\Gamma^0) \cdot \delta n_\mu(\Gamma^0) \cdot \overline{\delta n_\nu}(t|\Gamma^0) \\
&= \int d\Gamma^0 P_{\rm eq}(\Gamma^0)(n_\alpha(\Gamma^0) - n_{\alpha,\rm eq}) \cdot (n_\beta(\Gamma^0) - n_{\beta,\rm eq}) \cdot (n_\mu(\Gamma^0) - n_{\mu,\rm eq}) \int d\Gamma \, P(\Gamma, t|\Gamma^0)(n_\nu(\Gamma) - n_{\nu,\rm eq}),
\end{aligned}
\tag{19}
$$

$$
\begin{aligned}
&\langle \delta n_\alpha(0) \delta n_\beta(0) \delta n_\mu(t) \delta n_\nu(t) \rangle_{\rm eq} \\
&= \int d\Gamma^0 P_{\rm eq}(\Gamma^0) \delta n_\alpha(\Gamma^0) \cdot \delta n_\beta(\Gamma^0) \cdot \overline{\delta n_\mu \cdot \delta n_\nu}(t|\Gamma^0) \\
&= \int d\Gamma^0 P_{\rm eq}(\Gamma^0)(n_\alpha(\Gamma^0) - n_{\alpha,\rm eq}) \cdot (n_\beta(\Gamma^0) - n_{\beta,\rm eq}) \int d\Gamma \, P(\Gamma, t|\Gamma^0)(n_\mu(\Gamma) - n_{\mu,\rm eq}) \cdot (n_\nu(\Gamma) - n_{\nu,\rm eq}),
\end{aligned}
\tag{20}
$$

$$\langle \delta n_\alpha(0) \delta n_\beta(t) \delta n_\mu(t) \delta n_\nu(t) \rangle_{\rm eq}$$

$$= \int d\Gamma^0 P_{\rm eq}(\Gamma^0) \delta n_\alpha(\Gamma^0) \cdot \overline{\delta n_\beta \cdot \delta n_\mu \cdot \delta n_\nu}(t|\Gamma^0)$$

$$= \int d\Gamma^0 P_{\rm eq}(\Gamma^0)(n_\alpha(\Gamma^0) - n_{\alpha,\rm eq}) \int d\Gamma P(\Gamma, t|\Gamma^0)(n_\beta(\Gamma) - n_{\beta,\rm eq}) \cdot (n_\mu(\Gamma) - n_{\mu,\rm eq}) \cdot (n_\nu(\Gamma) - n_{\nu,\rm eq}). \quad (21)$$

Within the PG model, the fluctuations of phonon occupation numbers at two different modes are considered to be statistically independent at a thermal equilibrium, i.e., $< n_\alpha \cdot n_\beta >_{\rm eq} = n_{\alpha,\rm eq} \cdot n_{\beta,\rm eq}$ for $\alpha \neq \beta$. As a result, the values of the normalized time-correlation function at $t = 0$ are simply $c_{\alpha\beta}(t = 0) = \delta_{\alpha\beta}$, where $\delta_{\alpha\beta}$ is the Kronecker-δ symbol. Yet, the PG model does not state the value of a cross-correlation function [Eq. (16)] at any other time $t \neq 0$, except that $c_{\alpha\beta}(t) \to 0$ as $t \to \infty$. Multiple-mode correlation functions remain poorly understood, even within the PG model.

C. Ornstein-Uhlenbeck processes

The FPE for a well-studied class of stochastic processes, the so-called Ornstein-Uhlenbeck (OU) processes [56], can be solved analytically. To demonstrate the properties of these OU processes, we start with a new set of zero-mean and unit-variance stochastic variables $\tilde{\Gamma} = (x_1, x_2, x_3, \cdots, x_N)$, i.e., $\langle x_\lambda \rangle_{\rm eq} = 0$ and $\langle x_\lambda^2 \rangle_{\rm eq} = 1$. The OU processes are defined in terms of their specific form of drift and diffusion coefficients: $A_\lambda(\tilde{\Gamma}) = -\gamma_\lambda x_\lambda$ and $B_{\lambda\lambda'}(\tilde{\Gamma}) = 2\gamma_\lambda \delta_{\lambda,\lambda'}$, with $\gamma_\lambda > 0$. Consequently, the Fokker-Planck equation for OU-type processes can be rewritten in a separable multiple-variable partial differential equation:

$$\frac{\partial P(\tilde{\Gamma}, t|\tilde{\Gamma}^0)}{\partial t} = \sum_{\lambda=1}^N \gamma_\lambda \left[1 + x_\lambda \cdot \frac{\partial}{\partial x_\lambda} + \frac{\partial^2}{\partial x_\lambda^2} \right] P(\tilde{\Gamma}, t|\tilde{\Gamma}^0), \quad (22)$$

and its solution can be expressed as

$$P(\tilde{\Gamma}, t|\tilde{\Gamma}^0) = \prod_{\lambda=1}^N \frac{1}{\sqrt{2\pi \Delta_\lambda(t)}} e^{-\frac{[x_\lambda - \overline{x_\lambda}(t)]^2}{2\Delta_\lambda(t)}}, \quad (23)$$

where, $\overline{x_\lambda}(t) = x_\lambda(\tilde{\Gamma}^0) \cdot e^{-\gamma_\lambda t}$ and $\Delta_\lambda(t) = 1 - e^{-2\gamma_\lambda t}$. More details on the solution of an OU-type FPE can be found in Appendix B. Here we highlight one key result of the time-correlation between any two state variables x_λ and $x_{\lambda'}$ of an OU-type process:

$$\tilde{C}_{\lambda\lambda'}(t) = \langle x_\lambda(t') \cdot x_{\lambda'}(t' + t) \rangle_{\rm eq} = \delta_{\lambda,\lambda'} e^{-\gamma_\lambda t}. \quad (24)$$

More interesting results on the multiple variable correlation functions, such as the three-variable correlation functions: $\langle x_\lambda(t') \cdot x_{\lambda'}(t') \cdot x_{\lambda''}(t' + t) \rangle_{\rm eq}$, $\langle x_\lambda(t') \cdot x_{\lambda'}(t' + t) \cdot x_{\lambda''}(t' + t) \rangle_{\rm eq}$, and the four-variable correlation functions $\langle x_\lambda(t') \cdot x_{\lambda'}(t') \cdot x_{\lambda''}(t') \cdot x_{\lambda'''}(t' + t) \rangle_{\rm eq}$ and $\langle x_\lambda(t') \cdot x_{\lambda'}(t') \cdot x_{\lambda''}(t' + t) \cdot x_{\lambda'''}(t' + t) \rangle_{\rm eq}$, $\langle x_\lambda(t') \cdot x_{\lambda'}(t' + t) \cdot x_{\lambda''}(t' + t) \cdot x_{\lambda'''}(t' + t) \rangle_{\rm eq}$, are presented in Appendix B.

For a lattice vibration to be classified as an OU process, its set of drift coefficients $A(\Gamma)$ in the vibration FPE [Eq. (3)] must satisfy the following conditions:

$$A_\alpha(\Gamma) = -\sum_\beta \mathcal{D}_{\alpha\beta} \left(\frac{\Delta_{\alpha,\rm eq}}{\Delta_{\beta,\rm eq}} \right)^{1/2} (n_\beta - n_{\beta,\rm eq}),$$

$$\frac{d\overline{n_\alpha}(t|\Gamma^0)}{dt} = -\sum_\beta \mathcal{D}_{\alpha\beta} \left(\frac{\Delta_{\alpha,\rm eq}}{\Delta_{\beta,\rm eq}} \right)^{1/2} (\overline{n_\beta}(t|\Gamma^0)) - n_{\beta,\rm eq}). \quad (25)$$

Here $\mathcal{D}_{\alpha\beta}$ are matrix elements of the normalized drift matrix $\boldsymbol{\mathcal{D}}$, $n_{\alpha,\rm eq}$ and $\Delta_{\alpha,\rm eq}$ are, respectively, the equilibrium average value of the phonon number at αth mode and the corresponding statistical variance at the equilibrium with $\alpha, \beta = 1, 2, 3, \cdots, N$.

The $\boldsymbol{\mathcal{D}}$ matrix, as defined in Eq. (25), is a semipositive definite, real, and symmetric $N \times N$ matrix with a set of N eigenvalues γ_λ and corresponding normalized eigenvectors written as as $\vec{u}_\lambda = (u_{\lambda,1}, u_{\lambda,2}, u_{\lambda,3}, \cdots, u_{\lambda,N})$ for $\lambda = 1, 2, 3, \cdots, N$. We then can transform the N-dimensional phonon number state variables $\Gamma = \{n_1, n_2, \cdots, n_N\}$ into an equivalent set of zero-mean and unit-variance state variables $\tilde{\Gamma} = (x_1, x_2, x_3, \cdots, x_N)$ using this set of eigenvectors:

$$n_\alpha = n_{\alpha,\rm eq} + (\Delta_{\alpha,\rm eq})^{1/2} \sum_{\lambda=1}^N x_\lambda u_{\lambda,\alpha},$$

$$x_\lambda = \sum_{\alpha=1}^N \frac{n_\alpha - n_{\alpha,\rm eq}}{\Delta_{\alpha,\rm eq}^{1/2}} u_{\lambda,\rm eq}. \quad (26)$$

The linear transformation in Eqs. (26) also shows that the diffusion $B_{\alpha\beta}(\Gamma)$ coefficients for an OU-type lattice vibration are related to its drift coefficients $A_\alpha(\Gamma)$ through the $\mathcal{D}$ matrix:

$$B_{\alpha\beta}(\Gamma) = 2(\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} \sum_{\lambda=1}^{N} \gamma_\lambda u_{\lambda,\alpha} u_{\lambda,\beta} = 2(\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} \mathcal{D}_{\alpha\beta}. \tag{27}$$

In the rest of the paper, the $\mathcal{D}$ matrix is referred as the normalized drift/diffusion matrix.

Combining the results in Eqs. (16), (24), and (26), we can show that the normalized two-mode correlation functions $c_{\alpha\beta}(t)$ [Eq. (16)] in this OU-type lattice vibration are simply

$$c_{\alpha\beta}(t) = \sum_{\lambda=1}^{N} e^{-\gamma_\lambda t} u_{\lambda,\alpha} u_{\lambda,\beta}, \tag{28}$$

with $c_{\alpha\beta}(t=0) = \sum_{\lambda=1}^{N} u_{\lambda,\alpha} u_{\lambda,\beta} = \delta_{\alpha\beta}$. We can generalize the normalized two-mode correlation functions in Eq. (28) in an integral form:

$$c_{\alpha\beta}(t) = \int_0^\infty d\gamma \, \chi_{\alpha\beta}(\gamma) e^{-\gamma t}, \tag{29}$$

with $\chi_{\alpha\beta}(\gamma) = \sum_{\lambda=1}^{N} u_{\lambda,\alpha} u_{\lambda,\beta} \cdot \delta(\gamma - \gamma_\lambda)$. Equation (29) indicates that a mode correlation function $c_{\alpha\beta}(t)$ can be viewed as the t-space Laplace transformation of the γ-space function $\chi_{\alpha\beta}(\gamma)$. We refer to $\chi_{\alpha\beta}(\gamma)$ as the Laplace spectral function of $c_{\alpha\beta}(t)$. At the $N \to \infty$ limit, a Laplace spectral function $\chi_{\alpha\beta}(\gamma)$ converges to a continuous function defined in the spectral regime of $[0, \gamma_{\max}]$. The kth moment of a $\chi_{\alpha\beta}(\gamma)$ function, defined as $\mu_{\alpha\beta}(k) \equiv \int_0^\infty d\gamma \, \chi_{\alpha\beta}(\gamma) \cdot \gamma^k$, is given as

$$\mu_{\alpha\beta}(k) = \sum_{\lambda=1}^{N} u_{\lambda,\alpha} u_{\lambda,\beta} \gamma_\lambda^{\,k} = \langle \alpha | \mathcal{D}^k | \beta \rangle = (\mathcal{D}^k)_{\alpha\beta}. \tag{30}$$

The results in Eqs. (28) and (29) clearly demonstrate that in general the normalized mode self-correlation functions of lattice vibration do not decay as an exponential function of time, and the time-integral of the cross-correlation functions are not zero for two different modes. Some recent simulation studies [53] have reported their implementation based on fitting the MD simulated mode self-correlation functions based on an assumed formula of $C_{\alpha\beta}(t) \approx \Delta_{\alpha,\text{eq}} \cdot \delta_{\alpha,\beta} \cdot e^{-\gamma_\alpha t}$, and they reported the fitted decay factors γ_α as the inverse of phonon lifetimes $\tau_\alpha = \gamma_\alpha^{-1}$ in the PG model. For such a simplification to be valid, the normalized drift/diffusion matrix $\mathcal{D}$ has to be close to a diagonal matrix:

$$\mathcal{D} \approx \begin{bmatrix} \gamma_1 & 0 & 0 & \dots & 0 \\ 0 & \gamma_2 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & \gamma_N \end{bmatrix} \iff \mathcal{D}^{-1} \approx \begin{bmatrix} \tau_1 & 0 & 0 & \dots & 0 \\ 0 & \tau_2 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & \tau_N \end{bmatrix}. \tag{31}$$

However, the off-diagonal terms in the $\mathcal{D}$ matrix characterize the phonon-phonon mode scatterings, and they are usually not zero even within the approximation of the PG model. Similarly, the cross-correlation functions between two vibrational modes are usually not zero even within the approximation of the PG model.

The analytical solution of the probability function of an OU-type vibration FPE also predicts the time-correlation functions of multiple vibrational modes. For example, based on the derivation in Appendix B, all the correlation functions of odd-number vibrational modes are zero for an OU-type lattice. There are three types of four-mode correlation functions:

$$\langle \delta n_\alpha(0) \delta n_\beta(0) \delta n_\mu(0) \delta n_\nu(t) \rangle_{\text{eq}} = (\Delta_{\alpha,\text{eq}} \Delta_{\beta,\text{eq}} \Delta_{\mu,\text{eq}} \Delta_{\nu,\text{eq}})^{\frac{1}{2}} \cdot \sum_{\lambda\lambda'\lambda''\lambda'''} (u_{\lambda,\alpha} u_{\lambda',\beta} u_{\lambda'',\mu} u_{\lambda''',\nu}) \cdot \langle x_\lambda(0) \cdot x_{\lambda'}(0) \cdot x_{\lambda''}(0) \cdot x_{\lambda'''}(t) \rangle_{\text{eq}}$$

$$= (\Delta_{\alpha,\text{eq}} \Delta_{\beta,\text{eq}} \Delta_{\mu,\text{eq}} \Delta_{\nu,\text{eq}})^{\frac{1}{2}} \cdot [\delta_{\alpha\mu} c_{\beta\nu}(t) + \delta_{\beta\mu} c_{\alpha\nu}(t) + \delta_{\alpha\beta} c_{\mu\nu}(t)], \tag{32}$$

$$\langle \delta n_\alpha(0) \delta n_\beta(t) \delta n_\mu(t) \delta n_\nu(t) \rangle_{\text{eq}} = (\Delta_{\alpha,\text{eq}} \Delta_{\beta,\text{eq}} \Delta_{\mu,\text{eq}} \Delta_{\nu,\text{eq}})^{\frac{1}{2}} \cdot \sum_{\lambda\lambda'\lambda''\lambda'''} (u_{\lambda,\alpha} u_{\lambda',\beta} u_{\lambda'',\mu} u_{\lambda''',\nu}) \cdot \langle x_\lambda(0) \cdot x_{\lambda'}(t) \cdot x_{\lambda''}(t) \cdot x_{\lambda'''}(t) \rangle_{\text{eq}}$$

$$= (\Delta_{\alpha,\text{eq}} \Delta_{\beta,\text{eq}} \Delta_{\mu,\text{eq}} \Delta_{\nu,\text{eq}})^{\frac{1}{2}} \cdot [\delta_{\mu\nu} c_{\alpha\beta}(t) + \delta_{\beta\nu} c_{\alpha\mu}(t) + \delta_{\beta\mu} c_{\alpha\nu}(t)], \tag{33}$$

$$\langle \delta n_\alpha(0) \delta n_\beta(0) \delta n_\mu(t) \delta n_\nu(t) \rangle_{\text{eq}} = (\Delta_{\alpha,\text{eq}} \Delta_{\beta,\text{eq}} \Delta_{\mu,\text{eq}} \Delta_{\nu,\text{eq}})^{\frac{1}{2}} \cdot \sum_{\lambda\lambda'\lambda''\lambda'''} (u_{\lambda,\alpha} u_{\lambda',\beta} u_{\lambda'',\mu} u_{\lambda''',\nu}) \cdot \langle x_\lambda(0) \cdot x_{\lambda'}(0) \cdot x_{\lambda''}(t) \cdot x_{\lambda'''}(t) \rangle_{\text{eq}}$$

$$= (\Delta_{\alpha,\text{eq}} \Delta_{\beta,\text{eq}} \Delta_{\mu,\text{eq}} \Delta_{\nu,\text{eq}})^{\frac{1}{2}} \cdot [\delta_{\alpha\beta} \delta_{\mu\nu} + c_{\alpha\mu}(t) \cdot c_{\beta\nu}(t) + c_{\alpha\nu}(t) \cdot c_{\beta\mu}(t)], \tag{34}$$

with $c_{\alpha\beta}(t)$ being the normalized time-correlation function between αth mode and β-mode [Eqs. (16), (28), and (29), and the initial values of the four-mode time-correlation functions derived as $\langle \delta n_{\alpha}(0)\delta n_{\beta}(0)\delta n_{\mu}(0)\delta n_{\nu}(0)\rangle_{eq} = (\Delta_{\alpha,eq}\Delta_{\beta,eq}\Delta_{\mu,eq}\Delta_{\nu,eq})^{\frac{1}{2}} \cdot [\delta_{\alpha\beta}\delta_{\mu\nu} + \delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}]$.

III. LATTICE THERMAL CONDUCTIVITY

A. Green-Kubo theory

The fluctuation-dissipation theorem provides a general statistical theory to connect the equilibrium fluctuation processes of a macroscopic quantity, e.g., the total heat current vector $\vec{J} = (J_x, J_y, J_z)$ in a solid and the related irreversible transport processes, such as heat conduction at nonequilibrium conditions. Within the statistical linear response transport theory, the thermal conductivity tensor κ_{IJ}, with $I, J = x, y, z$ labeling the Cartesian axes, is expressed in the GK formula in terms of the time integral of the current-current correlation functions [43,44],

$$\kappa_{IJ} = \frac{1}{k_B T^2 \Omega N_{\text{cell}}} \int_0^{\infty} dt \langle J_I(0) J_J(t) \rangle_{\text{eq}}, \qquad (35)$$

where Ω and N_{cell} are, respectively, volume of the unit cell and total number of cells in a supercell model with the Born-von Karman periodic boundary.

At the atomistic level, the heat current $\vec{J}$ is a function of atomic forces, displacements, and momenta, and various approximations have been proposed and discussed [57]. Assuming the heat current vector is also a function of phonon numbers of modes, i.e., $\vec{J} = \vec{J}(\{\Gamma\}) = \vec{J}(n_1, n_2, n_3, \cdots, n_N)$, we can use Eq. (9) to evaluate the current-current correlation functions. Under the condition of small thermal fluctuation, the Cartesian components of the heat current vector can be simplified as

$$J_I \approx \sum_{\alpha} \frac{\partial J_I}{\partial \Delta n_{\alpha}} \Delta n_{\alpha} = \sum_i \Lambda_{I\alpha} \Delta n_{\alpha}. \qquad (36)$$

The seminal Peierls formula of the heat current of a PG, $\vec{J} = \sum_{\alpha} \Delta n_{\alpha} \hbar \omega_{\alpha} \vec{v}_{\alpha}$, is an approximation of this class, with $\Lambda_{I\alpha} = \hbar \omega_{\alpha} v_{\alpha I}$. When the higher order terms (also referred as the nonharmonic terms) in the J formula are included as the corrections to the linear terms formulated in Eq. (36), we can rewrite the J_I as $J_I = \sum_i \Lambda_{I\alpha} \Delta n_{\alpha} + \delta J_I$. Consequently, the current-current correlation functions can be expressed as

$$\langle J_I(0) J_J(t) \rangle_{\text{eq}} = \sum_{\alpha\beta} \Lambda_{I\alpha} \Lambda_{J\beta} \langle \Delta n_{\alpha}(0) \Delta n_{\beta}(t) \rangle_{\text{eq}}$$
$$+ \sum_{\alpha} \Lambda_{I\alpha} \langle \Delta n_{\alpha}(0) \delta J_J(t) \rangle_{\text{eq}}$$
$$+ \sum_{\alpha} \Lambda_{J\alpha} \langle \delta J_I(0) \Delta n_{\alpha}(t) \rangle_{\text{eq}}$$
$$+ \langle \delta J_I(0) \delta J_J(t) \rangle_{\text{eq}}. \qquad (37)$$

Wherever the nonharmonic $\delta \vec{J}$ terms in the vibrational heat current in a lattice are not negligible, time-correlation functions of multiple modes, such as the four-mode correlation functions shown in Eqs. (32), (33), (34), are needed to evaluate the current-current correlation function shown in Eq. (37). At the condition that the general linear approximation of Eq. (36) is valid, the time integral of $\langle J_I(0) J_J(t) \rangle_{\text{eq}}$ is approximated in terms of time integrals of normalized two-mode correlation functions $c_{\alpha\beta}(t)$:

$$\int_0^{\infty} dt \langle J_I(0) J_J(t) \rangle_{\text{eq}} \approx \sum_{\alpha\beta} \Lambda_{I\alpha} \Lambda_{J\beta} \int_0^{\infty} dt \langle \Delta n_{\alpha}(0) \Delta n_{\beta}(t) \rangle_{\text{eq}}$$
$$= \sum_{\alpha\beta} \Lambda_{I\alpha} \Lambda_{J\beta} (\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} \int_0^{\infty} dt\, c_{\alpha\beta}(t). \qquad (38)$$

Based on the GK formula, we now express κ_{Latt} in the form of

$$\kappa_{IJ} = \frac{1}{k_B T^2 \Omega N_{\text{Cell}}} \sum_{\alpha\beta} \Lambda_{I\alpha} \Lambda_{J\beta} (\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} \int_0^{\infty} dt\, c_{\alpha\beta}(t). \qquad (39)$$

As shown in Eq. (28) of Sec. II C, when a lattice vibration can be approximated as an OU process, the lattice thermal conductivity is simply

$$\kappa_{IJ} = \frac{1}{k_B T^2 \Omega N_{\text{Cell}}} \sum_{\alpha\beta} \Lambda_{I\alpha} \Lambda_{J\beta} (\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} \sum_{\lambda=1}^{N} \int_0^{\infty} dt\, e^{-\gamma_{\lambda} t} u_{\lambda,\alpha} u_{\lambda,\beta}$$
$$= \frac{1}{k_B T^2 \Omega N_{\text{Cell}}} \sum_{\alpha\beta} \Lambda_{I\alpha} \Lambda_{J\beta} (\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} \sum_{\lambda=1}^{N} (\gamma_{\lambda})^{-1} u_{\lambda,\alpha} u_{\lambda,\beta}$$
$$= \frac{1}{k_B T^2 \Omega N_{\text{Cell}}} \sum_{\alpha\beta} \Lambda_{I\alpha} \Lambda_{J\beta} (\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} (\mathcal{D})^{-1}_{\alpha\beta}. \qquad (40)$$

B. Phonon Boltzmann transport equation

As a kinetic transport theory, the phonon BTE theory is valid only within the PG approximation, i.e., at a thermal equilibrium, each mode oscillates at a harmonic frequency ω and the ensemble-averaged number of phonons at this mode follows the Bose-Einstein distribution $n_{eq}(\omega) = \langle n \rangle_{eq} = \frac{1}{e^{(\hbar\omega/k_B T)}-1}$ and $\Delta_{eq} = \langle n^2 \rangle_{eq} - \langle n \rangle_{eq}^2 = n_{eq} \cdot (n_{eq} + 1)$. In addition, the phonon BTE theory applies only to a crystalline solid, where each vibrational mode of this translation-invariant periodic lattice corresponds to a reciprocal-space $\vec{k}$ vector and a group velocity $\vec{v} = \vec{\nabla}_k(\omega)$.

When a constant temperature gradient $\vec{\nabla}_r T$ is imposed on the periodic lattice, the ensemble-averaged phonon numbers, n_α for $\alpha = 1, 2, 3, \cdots, N$, are no longer able to relax back to their original equilibrium values $n_{eq,\alpha}$ as a result of thermal diffusion. Instead, each n_α approaches a space-dependent value when a steady state is reached:

$$\left(\frac{\partial n_\alpha}{\partial t}\right) = -\left(\frac{dn_\alpha}{dt}\right)_{\text{diffusion}} - \left(\frac{dn_\alpha}{dt}\right)_{\text{scattering}} = 0, \quad (41)$$

where the diffusion term at the $\vec{\nabla}_r T \to 0$ limit is approximated as

$$\left(\frac{dn_\alpha}{dt}\right)_{\text{diffusion}} = -\vec{v}_\alpha \cdot \vec{\nabla}_r n_\alpha$$

$$\simeq -\frac{\hbar\omega_\alpha}{k_B T^2} n_{\alpha,eq}(n_{\alpha,eq} + 1)\vec{v}_\alpha \cdot \vec{\nabla}_r T. \quad (42)$$

A common approximation for the scattering terms in the phonon BTE [Eq. (41)] is the so-called linearized approximation:

$$\left(\frac{dn_\alpha}{dt}\right)_{\text{scattering}} \simeq -\sum_{\beta=1}^{N} \sqrt{\frac{n_{\alpha,eq} \cdot (n_{\alpha,eq} + 1)}{n_{\beta,eq} \cdot (n_{\beta,m} + 1)}} \cdot \mathcal{L}_{\alpha\beta} \cdot (n_\beta - n_{\beta,eq}), \quad (43)$$

where $\mathcal{L}$ is referred as the linear phonon-scattering matrix.

By using the results of Eqs. (42) and (43) and the definition of $\phi_\alpha \equiv \frac{n_\alpha - n_{\alpha,eq}}{\sqrt{n_{\alpha,eq} \cdot (n_{\alpha,eq}+1)}}$, the steady-state phonon Boltzmann equation [Eq. (41)] can be rewritten as a set of linear equations for ϕ_α with $\alpha = 1, 2, 3, \cdots, N$:

$$\sum_{\beta=1}^{N} \mathcal{L}_{\alpha\beta} \cdot \phi_\beta = -\frac{\hbar\omega_\alpha}{k_B T^2} \sqrt{n_{\alpha,eq}(n_{\alpha,eq} + 1)}\vec{v}_\alpha \cdot \vec{\nabla}_r T. \quad (44)$$

Similar to what we have derived in Sec. II C, we can solve the set of linear equations using the eigenvectors and the eigenvalues of the matrix $\boldsymbol{L}$:

$$\phi_\alpha = -\sum_{\lambda=1}^{N} \gamma_\lambda^{-1} u_{\lambda,\alpha} \sum_{\beta=1}^{N} \frac{\hbar\omega_\beta}{k_B T^2} \sqrt{n_{\beta,eq}(n_{\beta,eq} + 1)}(\vec{v}_\beta \cdot \vec{\nabla}_r T) u_{\lambda,\beta}$$

$$= -\sum_{\beta=1}^{N} \left(\sum_{\lambda=1}^{N} \gamma_\lambda^{-1} u_{\lambda,\alpha} u_{\lambda,\beta}\right) \cdot \frac{\hbar\omega_\beta}{k_B T^2} \sqrt{n_{\beta,eq}(n_{\beta,eq} + 1)}(\vec{v}_\beta \cdot \vec{\nabla}_r T) \quad (45)$$

$$= -\sum_{\beta=1}^{N} (\mathcal{L})_{\alpha\beta}^{-1} \cdot \frac{\hbar\omega_\beta}{k_B T^2} \sqrt{n_{\beta,eq}(n_{\beta,eq} + 1)}(\vec{v}_\beta \cdot \vec{\nabla}_r T),$$

where γ_λ and $\vec{u}_\lambda$ are the λth eigenvalue and eigenvector of the matrix $\mathcal{L}$, and $(\mathcal{L})^{-1}$ represents the inverse matrix of $\mathcal{L}$.

Based on the Peierls formula for the heat current of a PG, the lattice thermal conductivity predicted by the linearized phonon BTE theory can be expressed as

$$\kappa_{IJ} = \frac{1}{\Omega N_{\text{Cell}}} \sum_{\alpha\beta} (\boldsymbol{L})_{\alpha\beta}^{-1} \cdot \frac{\sqrt{n_{\alpha,eq}(n_{\alpha,eq} + 1)}\sqrt{n_{\beta,eq}(n_{\beta,eq} + 1)}\hbar\omega_\alpha\hbar\omega_\beta}{k_B T^2} v_{\alpha I} \cdot v_{\beta J}$$

$$= \frac{1}{\Omega N_{\text{Cell}}} \sum_{\alpha\beta} (c_\alpha c_\beta)^{1/2} \cdot v_{\alpha I} \cdot v_{\beta J} \cdot (\boldsymbol{L})_{\alpha\beta}^{-1}, \quad (46)$$

where $c = k_B \cdot (\frac{\hbar\omega}{k_B T})^2 \cdot n_{\alpha,eq} \cdot (n_{\alpha,eq} + 1)$ is the single-mode heat capacity.

To compare κ_{Latt} predicted by the phonon BTE [Eq. (46)] and the one by the OU-type vibration FPE [Eq. (40)], we first note that in the limit of weak phonon scattering of the PG model, the variance of the phonon number fluctuation

of a mode $\Delta_{\alpha,eq}$ has already been shown to converge to the value of $n_{\alpha,eq} \cdot (n_{\alpha,eq} + 1)$, and the Peierls formula of heat current is valid. Furthermore, with the interpretation of phonon occupation number n_α in the phonon BTE as the time-dependent expectation value of the phonon number during the thermal relaxation process, we conclude that the

normalized drift/diffusion matrix $\mathcal{D}$ in an OU-type vibration FPE [Eq. (25)] is identical to the linear phonon-scattering matrix $\mathcal{L}$, i.e., $\mathcal{D} \rightarrow \mathcal{L}$, at the weak phonon-scattering limit of the PG approximation. Consequently, κ_{Latt} predicted by the vibration FPE [Eq. (40)] converges to that predicted by the conventional phonon BTE [Eq. (46)]. The so-called single mode relaxation approximation (SMRA) or relaxation time approximation (RTA) of a kinetic transport model corresponds to the cases where the phonon-scattering matrix $\mathcal{L}$ (or the drift/diffusion matrix ($\mathcal{D}$) can be treated as a semipositively defined diagonal matrix [Eq. (31)].

C. Discussions and future applications

A comparison chart is shown in Table I to highlight commonality and distinction between the atomistic MD simulation method and the vibration FPE. The MD simulation approach has an absolute advantage in simulating the atomistic scale lattice heat currents at moderate and high temperature, and it applies consistently to disordered solids, very anharmonic solids, as well as fluids. However, MD simulations only provide a semiquantitative description of the fluctuation properties of individual vibrational modes based on the damped oscillator model. First, corrections to the quantized lattice vibration have to be considered at low temperature because of the classical nature of MD simulations. Second, the mode lifetimes extracted from the numerical solutions of MD trajectories over long simulation periods reflect only partial information on the fluctuation and relaxation processes in lattice dynamics. Because of the assumption that all the cross-mode correlation functions between two different vibrational modes are zero, the DOA is equivalent to the SMRA or RTA in kinetic transport theories. The predicted κ_{Latt} from these approximate kinetic theories are known to be noticeably underestimated compared to those derived from the full solutions of the phonon BTE theory at low temperature [4,23] or in low-dimension materials [27].

In contrast, the vibration FPE approach complements the conventional MD simulation approach for conditions in which the interactions among vibrational modes are moderate, and it can be adopted to delineate the breakdown conditions of the PG model in MD simulations. Based on vibration FPE, we propose that the PG model applies when the OU approximation of the drift and diffusion coefficients [Eqs. (25) and (27)] is valid. By considering the normalized drift/diffusion $\mathcal{D}$ matrix in an OU-type vibration FPE equivalent to the scattering $\mathcal{L}$ matrix in a phonon BTE, we have proved that the κ_{Latt} derived from the linear response transport theory converges to that from the kinetic transport theory within the PG approximation.

When the interactions among vibrational modes are perturbatively small, the normalized drift/diffusion $\mathcal{D}$ matrix can be derived by using quantum perturbation theories for lattice vibration at low temperature. As temperature elevates to the semiclassical and classical regimes, we can implement numerical algorithms to directly compute normalized drift/diffusion coefficients with first-principles MD simulations. As these coefficients are defined in the short-time limit, high-performance parallel computer platforms can be utilized to distribute the computational loads of such simulations in parallel. When the temperature dependence of the drift/diffusion coefficients are extracted and tested with the OU approximation, we are able to not only quantitatively determine the temperature condition in which the PG model breaks down, but also identify the individual vibrational modes that lead to the breakdown.

IV. CONCLUSIONS

In summary, we have developed a vibration Fokker-Planck equation theory to describe stochastic lattice dynamics in solids. Instead of simulating the atomic trajectories using the MD methods, this statistical theory characterizes the fluctuation and relaxation processes in terms of a time-dependent, multiple-mode probability function, evolving from a thermally sampled single microstate at $t = 0$ [Eq. (1)] to the equilibrium distribution over all the accessible microstates as $t \rightarrow \infty$ [Eq. (2)]. The dynamical properties that govern the stochastic processes at atomistic scale are coarse-grained into two sets of parameters of a vibration FPE, the drift A and diffusion B coefficients of vibrational modes [Eqs. (3) and (4)]. At the limit of weak mode-mode interactions, these coefficients can be derived with quantum perturbation theories, such as Fermi's golden rule [Eqs. (5) and (6)]. Beyond the perturbation approximation, these coefficients can be directly computed by using MD methods over short simulation time periods (i.e., $\delta t \approx 0$). Thus, the intensive computational loads of sampling a large amount of initial microstates of a vibrating lattice can be distributed in a computer platform with massive parallel algorithms.

Our time-dependent probability theory presents a new paradigm to compute correlation functions among vibrational modes [Eqs. (16) and (17)]. The advantage of this statistical approach is clearly demonstrated at the OU condition (Sec. II C), in which the vibration FPE has an analytical solution [Eqs. (23)–(26)] and the correlation functions among multiple modes [Eqs. (28), (32)–(34)] can be derived in terms of eigenvalues and eigenvectors of the normalized drift/diffusion matrix $\mathcal{D}$ [Eqs. (25) and (27)]. By equating the $\mathcal{D}$ matrix in an OU-type vibration FPE with the conventional phonon-scattering matrix $\mathcal{L}$ [Eq. (43)] in a phonon BTE, we have presented rigorous mathematical proof to equalize κ_{Latt} results from both the GK theory [Eq. (40)] and the BTE theory [Eq. (46)] with the Peierls harmonic heat current formula [Eq. (36)].

Although both the vibration FPE theory and the phonon BTE theory predict identical κ_{Latt} results within the PG model, the vibration FPE provides additional theoretical insight on the heat conduction mechanism at microscopic level. First, the vibration FPE theory quantitatively defines the contributions to the overall κ_{Latt} from both the self-correlation functions of individual modes and the cross-correlation functions between two different modes [Eq. (39)]. Second, the vibration FPE further predicts all the multiple-mode correlation functions, which can be analyzed in the future to account for effects of anharmonic correction terms in heat flux [28,57]. Finally, when perturbation theories become insufficient to evaluate the phonon-scattering matrix $\mathcal{L}$ of a phonon BTE, the full set of matrix elements of $\mathcal{L}$, instead of merely effective phonon lifetimes, can be computed as the normalized drift/diffusion

TABLE I. Comparison chart for the molecular dynamics method and the vibration Fokker-Planck equation method.

	Molecular dynamics simulation	Fokker-Plank equation
Thermal conductivity κ	*Green-Kubo formula:* $\kappa_{IJ} = \dfrac{1}{\Omega k_B T^2} \displaystyle\int_0^\infty \langle J_\alpha(0) J_\beta(t) \rangle_{eq}\, dt$ *with $J(t)$ as the fluctuating heat current* *Required input: The time-correlation function of heat current* $\langle J_\alpha(0) J_\beta(t) \rangle_{eq}$.	
Heat current J	$J = \dfrac{1}{2} \displaystyle\sum_i \sum_{j>i} \mathbf{F}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j)(\mathbf{r}_i - \mathbf{r}_j)$ $\mathbf{r}_i, \mathbf{v}_i \sim atomic\ position/velocity$ $\mathbf{F}_{ij} \sim force\ between\ two\ atoms$ *Classical Newton's second law*	$J(\{n_1, n_2, \cdots, n_N\}) = \mathbf{J}_0 + \Delta\mathbf{J},\ n \sim phonon\ numbers$ *Harmonic heat current:* $J_0 = \sum_\alpha n_\alpha \hbar\omega_\alpha \mathbf{v}_{g\alpha},\ (\omega, v_g) \sim frequency/group\ velocity$ *Anharmonic heat current:* $\Delta\mathbf{J} \to beyond\ the\ Perierls\ approximation, not\ yet\ formulated$
Dynamics	$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} V(\mathbf{r}_1, \cdots, \mathbf{r}_n)$ $V \sim many-body\ inter-atomic\ potential$ *Damped oscillators and mode lifetimes* $V = V_{harmonic} + \Delta V_{anh},\ \Delta V_{anh} \gg V_{harmonic}$ *Only numerical solution for* $\mathbf{r}_i(t), \mathbf{v}_i(t)$ *Normal mode analysis:*	*Quantum, semiclassical, and classical* $A_\alpha(\Gamma) \equiv \lim_{\delta t \to 0} \dfrac{1}{\delta t} \displaystyle\int_0^{\delta t} d\Gamma'\, \delta n_\alpha(\Gamma, \Gamma') P(\Gamma', \delta t|\Gamma)$ $B_{\alpha\beta}(\Gamma) \equiv \lim_{\delta t \to 0} \dfrac{1}{\delta t} \displaystyle\int_0^{\delta t} d\Gamma'\, \delta n_\alpha(\Gamma, \Gamma') \delta n_\beta(\Gamma, \Gamma') P(\Gamma', \delta t|\Gamma)$ *OU Approximation of drift/diffusuion coefficients* $\Longleftrightarrow$ *phonon gas model* $A_\alpha(\Gamma) = -\sum_\beta \mathcal{D}_{\alpha\beta} \sqrt{\Delta_{\alpha,eq}/\Delta_{\beta,eq}}\, \delta n_\beta,\ B_{\alpha\beta}(\Gamma) = 2\sqrt{\Delta_{\alpha,eq} \cdot \Delta_{\beta,eq}}\, \mathcal{D}_{\alpha\beta}$ *Analytical solution:* $P(\tilde{\Gamma}, t|\tilde{\Gamma}^0) = \prod_{\lambda=1}^N \dfrac{1}{\sqrt{2\pi \Delta_\lambda(t)}} e^{-\frac{|x_\lambda - \overline{x}_\lambda(t)|^2}{2\Delta_\lambda(t)}}$ *Analytical formulas of multiple-mode time-correlation function:*
Phonon	— Long simulation time is necessary	— Two-mode: $c_{\alpha\beta} = \langle \delta n_\alpha(0) \cdot \delta n_\beta(t) \rangle_{eq} / \sqrt{\langle \delta n_\alpha^2 \rangle_{eq} \cdot \langle \delta n_\beta^2 \rangle_{eq}}$ $= \displaystyle\sum_{\lambda=1}^N e^{-\gamma_\lambda t} u_{\lambda,\alpha} u_{\lambda,\beta} \Rightarrow \int_0^\infty d\gamma\, \chi_{\alpha\beta}(\gamma) e^{-\gamma t}$ with $N \to \infty$
Gas	— Self-correlation functions $c_{\alpha\alpha}(t)$ often assumed to be e^{-t/τ_α}	— Three-mode: $\langle \delta n_\alpha(0)\delta n_\beta(0)\delta n_\mu(t) \rangle_{eq} = 0$
Limit	— Cross correlations $c_{\alpha\beta}(t)$ often assumed to be zero — Three/four-mode correlation functions rarely discussed	— Four-mode: $\langle \delta n_\alpha(0)\delta n_\beta(0)\delta n_\mu(0)\delta n_\nu(t) \rangle_{eq} =$ $[\delta_{\alpha\mu} c_{\beta\nu}(t) + \delta_{\beta\mu} c_{\alpha\nu}(t) + \delta_{\alpha\beta} c_{\mu\nu}(t)] \sqrt{\langle \delta n_\alpha^2 \rangle_{eq} \langle \delta n_\beta^2 \rangle_{eq} \langle \delta n_\mu^2 \rangle_{eq} \langle \delta n_\nu^2 \rangle_{eq}}$

coefficients of an OU-type FPE by using the MD simulations over short-time periods.

To study the mechanisms of lattice heat conduction beyond the PG model, it is critical to establish a quantatitive criterion that delineates the breakdown conditions. The theoretical analysis presented in this paper indicates that the OU condition of stochastic lattice dynamics [Eqs. (25) and (27)] might serve as such breakdown criterion. We are currently implementing MD methods to compute the temperature-dependent drift/diffusion coefficients up to the melting temperature of a lattice. Various numerical methods, such as adiabatic elimination of variables method, matrix continued-fraction method, or variational methods, will be examined to solve the vibration FPE beyond the OU approximation [55]. It is promising that this vibration FPE presents a new theoretical framework to accurately and effectively predict the stochastic vibrational processes and the thermal transport properties of solids within and beyond the PG model.

APPENDIX A: EXPECTATION VALUES AND STATISTICAL VARIANCES OF NUMBERS OF PHONONS

This Appendix provides some derivation details on some formulas about the expectation values and statistical variances of the phonon numbers shown in Sec. II.

We first define the time-dependent expectation values of the following three quantities using the ensemble averaged approach shown in Sec. II B:

$$\overline{n}_\alpha(t|\Gamma^0) \equiv \langle n_\alpha \rangle = \int d\Gamma\, n_\alpha P(\Gamma; t), \tag{A1}$$

$$\overline{n_\alpha n_\beta}(t|\Gamma^0) \equiv \langle n_\alpha n_\beta \rangle = \int d\Gamma\, n_\alpha n_\beta P(\Gamma; t), \tag{A2}$$

$$\overline{\Delta}_{\alpha\beta}(t|\Gamma^0) = \langle n_\alpha n_\beta \rangle - \langle n_\alpha \rangle \langle n_\beta \rangle. \tag{A3}$$

Using the vibration FPE shown in Eq. (3), we then prove that the first-order t-derivatives of these three quantities in Eqs. (A1) to (A2) have the following forms:

$$\frac{d\overline{n}_\alpha}{dt} = \int d\Gamma\, n_\alpha \frac{\partial}{\partial t} P(\Gamma, t|\Gamma^0)$$

$$= -\sum_i \int d\Gamma\, n_\alpha \frac{\partial}{\partial n_i}[A_i(\Gamma) \cdot P(\Gamma, t|\Gamma^0)] + \frac{1}{2}\sum_{ij} \int d\Gamma\, n_\alpha \frac{\partial^2}{\partial n_i \partial n_j}[B_{ij}(\Gamma) \cdot P(\Gamma, t|\Gamma^0)]. \tag{A4}$$

For $\alpha \neq i$, we have $\int d\Gamma\, n_\alpha \frac{\partial}{\partial n_i}[A_i(\Gamma)P(\Gamma, t|\Gamma^0)] = 0$. Similarly, $\int d\Gamma\, n_\alpha \frac{\partial}{\partial n_i}\frac{\partial}{\partial n_j}[B_{ij}(\Gamma)P(\Gamma, t|\Gamma^0)] = 0$ for $\alpha \neq i$ or $\beta \neq j$. As a result, Eq. (A4) is now simplified as

$$\frac{d\overline{n}_\alpha(t|\Gamma^0)}{dt} = -\int d\Gamma\, n_\alpha \frac{\partial}{\partial n_\alpha}(A_\alpha \cdot P) + \frac{1}{2}\int d\Gamma\, n_\alpha \frac{\partial^2}{\partial n_\alpha \partial n_\alpha}(B_{\alpha\alpha} \cdot P), \tag{A5}$$

with $\int d\Gamma\, n_\alpha \frac{\partial}{\partial n_\alpha}(A_\alpha \cdot P) = \int d\Gamma \frac{\partial}{\partial n_\alpha}(n_\alpha \cdot A_\alpha \cdot P) - \int d(\Gamma A_\alpha \cdot P) = -\int d\Gamma A_\alpha(\Gamma) \cdot P(\Gamma, t|\Gamma^0) = -\overline{A_\alpha}(t|\Gamma^0)$, and $\int d\Gamma\, n_\alpha \frac{\partial}{\partial n_\alpha}\frac{\partial}{\partial n_\alpha}(B_{\alpha\alpha} \cdot P) = \int d\Gamma \frac{\partial}{\partial n_\alpha}[n_\alpha \frac{\partial}{\partial n_\alpha}(B_{\alpha\alpha}P)] - \int d\Gamma \frac{\partial}{\partial n_\alpha}(B_{\alpha\alpha}P) = 0$. We now get

$$\frac{d\overline{\alpha}(t|\Gamma^0)}{dt} = \overline{A_\alpha}(t|\Gamma^0). \tag{A6}$$

Similarly, we can show that

$$\frac{d\overline{n_\alpha n_\beta}(t|\Gamma^0)}{dt} = \overline{n_\alpha A_\beta}(t|\Gamma^0) + \overline{n_\beta A_\alpha}(t|\Gamma^0) + \overline{B_{\alpha\beta}}(t|\Gamma^0). \tag{A7}$$

Consequently, we also have

$$\frac{d\overline{\Delta}_{\alpha\beta}(t|\Gamma^0)}{dt} = \frac{d\overline{n_\alpha n_\beta}(t|\Gamma^0)}{dt} - \overline{n}_\alpha(t|\Gamma^0) \cdot \frac{d\overline{n}_\beta(t|\Gamma^0)}{dt} - \overline{n}_\beta(t|\Gamma^0) \cdot \frac{d\overline{n}_\alpha(t|\Gamma^0)}{dt}$$

$$= \overline{B_{\alpha\beta}}(t|\Gamma^0) + [\overline{n_\alpha A_\beta}(t|\Gamma^0) - \overline{n}_\alpha(t|\Gamma^0) \cdot \overline{A_\beta}(t|\Gamma^0)] + [\overline{n_\beta A_\alpha}(t|\Gamma^0) - \overline{n}_\beta(t|\Gamma^0) \cdot \overline{A_\alpha}(t|\Gamma^0)]. \tag{A8}$$

APPENDIX B: ANALYTICAL SOLUTIONS OF THE FPE FOR AN OU PROCESS

In this Appendix, we verify the analytical solutions of an OU-type FPE [Eq. (22)] shown in Sec. II C. For a probability function of one stochastic variable x with zero-mean and unit variance, the corresponding OU-type FPE can be given as

$$\frac{\partial P(x,t)}{\partial t} = \gamma \cdot \left(1 + x \cdot \frac{\partial}{\partial x} + \frac{\partial^2}{\partial^2 x} \right) P(x,t). \tag{B1}$$

With $\frac{d}{dt}\overline{x} = -\gamma\overline{x}$, $\frac{d}{dt}\overline{x^2} = 2\gamma(1 - \overline{x^2})$, and the initial values $\overline{x}$ and $\overline{x^2}$ being x_0 and $(x_0)^2$ respectively, we have

$$\begin{aligned} \overline{x} &= x_0 e^{-\gamma t}, \\ \Delta &= \overline{x^2} - \overline{x}^2 = 1 - e^{-2\gamma t}. \end{aligned} \tag{B2}$$

We skip the details of derivation and only show that the analytical solution of Eq. (B1) is given as

$$P(x,t) = \frac{1}{\sqrt{2\pi \Delta(t)}} e^{-\frac{(x-\overline{x}(t))^2}{2\Delta(t)}}. \tag{B3}$$

Using the analytical solution in Eq. (B3), we can show that $\frac{\partial P(x,t)}{\partial t}$ on the left-hand side of Eq. (B1) is

$$\begin{aligned} \frac{\partial P(x,t)}{\partial t} &= \frac{\partial\left[\frac{1}{\sqrt{2\pi\Delta(t)}}\right]}{\partial t} e^{-\frac{(x-\overline{x}(t))^2}{2\Delta(t)}} + \frac{1}{\sqrt{2\pi\Delta(t)}} \frac{\partial\left[e^{-\frac{(x-\overline{x}(t))^2}{2\Delta(t)}}\right]}{\partial t} \\ &= \gamma[1 - \Delta^{-1}(t)]P(x,t) + \gamma\left[\frac{(x-\overline{x}(t))^2}{\Delta^2(t)} - \frac{x \cdot (x-\overline{x}(t))}{\Delta(t)}\right]P(x,t) \\ &= \gamma[1 - \Delta^{-1}(t) \cdot (1 - x\overline{x}(t) + x^2) + \Delta^{-2}(t) \cdot (x - \overline{x}(t))^2]P(x,t). \end{aligned} \tag{B4}$$

From the analytical solution in Eq. (B2), we also have $\frac{\partial P(x,t)}{\partial x} = -\Delta^{-1}(t) \cdot (x - \overline{x}(t)) \cdot P(x,t)$ and $\frac{\partial^2 P(x,t)}{\partial x^2} = -\Delta^{-1}(t) + \Delta^{-2}(t) \cdot (x - \overline{x}(t))^2 \cdot P(x,t)$. These results give us the right-hand side of Eq. (B1) in the form of

$$\gamma \cdot \left[1 + x \cdot \frac{\partial}{\partial x} + \frac{\partial^2}{\partial^2 x} \right] P(x,t) = \gamma \cdot [1 - x \cdot \Delta^{-1}(t) \cdot (x - \overline{x}(t)) - \Delta^{-1}(t) + \Delta^{-2}(t) \cdot (x - \overline{x}(t))^2] \cdot P(x,t)$$

$$= \gamma \cdot [1 - \Delta^{-1}(t) \cdot (1 - x \cdot \overline{x}(t) + x^2) + \Delta^{-2}(t) \cdot (x - \overline{x}(t))^2] \cdot P(x,t). \tag{B5}$$

With both Eqs. (B4) and (B5), we now verify that the probability function in Eq. (B3) is indeed the analytical solution of Eq. (B1).

For the case $N > 1$, the N-dimensional probability function of an OU-type FPE [Eq. (22)] can be expressed in a separable form $P(\tilde{\Gamma}, t) = \prod_{\lambda=1}^{N} f_\lambda(x_\lambda, t)$, and one N-variable FPE [Eq. (22)] is converted into N sets of partial differential equations:

$$\frac{\partial f_\lambda(x,t)}{\partial t} = \gamma_\lambda \cdot \left(1 + x_\lambda \cdot \frac{\partial}{\partial x_\lambda} + \frac{\partial^2}{\partial^2 x_\lambda} \right) f_\lambda(x,t), \tag{B6}$$

where $\lambda = 1, 2, 3, \cdots N$. Similar to the solution shown in Eq. (B3), we have the N sets of solutions of $f_\lambda(x,t) = (2\pi\Delta_\lambda)^{-1/2} \cdot e^{-\frac{(x_\lambda - \overline{x_\lambda})^2}{2\Delta_\lambda}}$, with $\overline{x_\lambda} = x_{\lambda,0}e^{-\gamma_\lambda t}$ and $\Delta_\lambda = 1 - e^{-2\gamma_\lambda t}$. Plugging these results in the separable multiple-variable formula, we now can verify that the analytical solution of Eq. (22) is indeed the probability function shown in Eq. (23).

The analytical solutions of the probability function for an OU-type FPE allows us to directly derive the correlation functions among these state variables with zero-means and unit variances. For example, the time-correlation functions between any two stochastic variables can be shown as the following familiar forms:

$$\begin{aligned} \langle x_\lambda(t') \cdot x_{\lambda'}(t' + t) \rangle_{\text{eq}} &= \langle x_\lambda(0) \cdot x_{\lambda'}(t) \rangle_{\text{eq}} \\ &= \langle x_\lambda \cdot x_{\lambda'} \rangle_{\text{eq}} e^{-\gamma_{\lambda'}t} = \delta_{\lambda,\lambda'} e^{-\gamma_\lambda t}. \end{aligned} \tag{B7}$$

Meanwhile, we can prove that all three-variable correlation functions for a multiple variable OU process zero:

$$\begin{aligned} \langle x_\lambda(0) \cdot x_{\lambda'}(0) \cdot x_{\lambda''}(t) \rangle_{\text{eq}} &= \langle x_\lambda \cdot x_{\lambda'} \cdot x_{\lambda''} \rangle_{\text{eq}} e^{-\gamma_{\lambda''}t} \\ &= 0 \cdot e^{-\gamma_{\lambda''}t} = 0, \end{aligned} \tag{B8}$$

$$\begin{aligned} \langle x_\lambda(t) \cdot x_{\lambda'}(0) \cdot x_{\lambda''}(t) \rangle_{\text{eq}} &= \langle x_\lambda \cdot x_{\lambda'} \cdot x_{\lambda''} \rangle_{\text{eq}} e^{-2\gamma_{\lambda''}t} + \langle x_\lambda \rangle_{\text{eq}} \cdot (1 - e^{-2\gamma_{\lambda''}t}) \cdot \delta_{\lambda'\lambda''} \\ &= 0 \cdot e^{-2\gamma_{\lambda''}t} + 0 \cdot (1 - e^{-2\gamma_{\lambda''}t}) \cdot \delta_{\lambda'\lambda''} = 0. \end{aligned} \tag{B9}$$

We can further generalize that the correlation functions of odd-number variables, such as three-variable, five-variable, etc., are all zero. Meanwhile, the correlation functions of even-number variables are not always zero. For example, for four-variable correlation functions, we have the following free formula:

$$
\langle x_\lambda(0) \cdot x_{\lambda'}(0) \cdot x_{\lambda''}(0) \cdot x_{\lambda'''}(t) \rangle_{\text{eq}} = \langle x_\lambda \cdot x_{\lambda'} \cdot x_{\lambda''} \cdot x_{\lambda'''} \rangle_{\text{eq}} e^{-\gamma_{\lambda'''}t}
$$
$$
= (\delta_{\lambda\lambda'''} \cdot \delta_{\lambda'\lambda''} + \delta_{\lambda'\lambda'''} \cdot \delta_{\lambda\lambda''} + \delta_{\lambda''\lambda'''} \cdot \delta_{\lambda\lambda'}) e^{-\gamma_{\lambda'''}t}, \tag{B10}
$$

$$
\langle x_\lambda(0) \cdot x_{\lambda'}(t) \cdot x_{\lambda''}(t) \cdot x_{\lambda'''}(t) \rangle_{\text{eq}} = \langle x_\lambda \cdot x_{\lambda'} \cdot x_{\lambda''} \cdot x_{\lambda'''} \rangle_{\text{eq}} e^{-(\gamma_{\lambda'}+\gamma_{\lambda''}+\gamma_{\lambda'''})t} + \langle x_\lambda x_{\lambda'} \rangle_{\text{eq}} \cdot e^{-\gamma_{\lambda'}t} \cdot (1 - e^{-2\gamma_{\lambda'}t}) \cdot \delta_{\lambda''\lambda'''}
$$
$$
+ \langle x_\lambda x_{\lambda''} \rangle_{\text{eq}} \cdot e^{-\gamma_{\lambda''}t} \cdot (1 - e^{-2\gamma_{\lambda'}t}) \cdot \delta_{\lambda'\lambda'''} + \langle x_\lambda x_{\lambda'''} \rangle_{\text{eq}} \cdot e^{-\gamma_{\lambda'''}t} \cdot (1 - e^{-2\gamma_{\lambda'}t}) \cdot \delta_{\lambda'\lambda''}
$$
$$
= (\delta_{\lambda\lambda'} \cdot \delta_{\lambda''\lambda'''} + \delta_{\lambda\lambda''} \cdot \delta_{\lambda'\lambda'''} + \delta_{\lambda\lambda'''} \cdot \delta_{\lambda'\lambda''}) \cdot e^{-(\gamma_{\lambda'}+\gamma_{\lambda''}+\gamma_{\lambda'''})t}
$$
$$
+ e^{-\gamma_\lambda t} \cdot [\delta_{\lambda\lambda'} \cdot \delta_{\lambda''\lambda'''} \cdot (1 - e^{-2\gamma_{\lambda'}t}) + \delta_{\lambda\lambda''} \cdot \delta_{\lambda'\lambda'''} \cdot (1 - e^{-2\gamma_{\lambda'}t}) + \delta_{\lambda\lambda'''} \cdot \delta_{\lambda'\lambda''} \cdot (1 - e^{-2\gamma_{\lambda'}t})]
$$
$$
= (\delta_{\lambda\lambda'} \cdot \delta_{\lambda''\lambda'''} + \delta_{\lambda\lambda''} \cdot \delta_{\lambda'\lambda'''} + \delta_{\lambda\lambda'''} \cdot \delta_{\lambda'\lambda''}) e^{-\gamma_\lambda t}, \tag{B11}
$$

$$
\langle x_\lambda(0) \cdot x_{\lambda'}(0) \cdot x_{\lambda''}(t) \cdot x_{\lambda'''}(t) \rangle_{\text{eq}} = \langle x_\lambda \cdot x_{\lambda'} \cdot x_{\lambda''} \cdot x_{\lambda'''} \rangle_{\text{eq}} e^{-(\gamma_{\lambda''}+\gamma_{\lambda'''})t} + \langle x_\lambda x_{\lambda'} \rangle_{\text{eq}} \cdot (1 - e^{-2\gamma_{\lambda''}t}) \cdot \delta_{\lambda''\lambda'''}
$$
$$
= (\delta_{\lambda\lambda''} \cdot \delta_{\lambda'\lambda'''} + \delta_{\lambda\lambda''} \cdot \delta_{\lambda'\lambda''} + \delta_{\lambda\lambda'} \cdot \delta_{\lambda''\lambda'''}) e^{-(\gamma_{\lambda''}+\gamma_{\lambda'''})t} + \delta_{\lambda\lambda'} \cdot \delta_{\lambda''\lambda'''} \cdot (1 - e^{-2\gamma_{\lambda''}t})
$$
$$
= \delta_{\lambda\lambda'} \cdot \delta_{\lambda''\lambda'''} + (\delta_{\lambda\lambda''} \cdot \delta_{\lambda'\lambda'''} + \delta_{\lambda\lambda'''} \cdot \delta_{\lambda'\lambda''}) e^{-(\gamma_\lambda+\gamma_{\lambda'})t}. \tag{B12}
$$

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