# Temperature-Dependent Classical Phonons from Efficient Nondynamical Simulations

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We present a method to calculate classical lattice-dynamical quantities, such as the temperature-dependent vibrational spectrum, from simulations that do not require an explicit solution of the time evolution. We start from the moment expansion of the relevant time-correlation function for a many-body system and show that it can be conveniently rewritten by using a basis in which the low-order moments are diagonal. This allows us to approximate the main spectral features (i.e., position and width of the phonon peaks) from thermal averages available from any statistical simulation. We illustrate our method with an application to a model system that presents a structural transition and strongly temperature-dependent phonons. Our theory also clarifies the status of previous heuristic schemes to estimate phonon frequencies.

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Is it possible to compute any equilibrium property of a material from appropriate thermal averages? From an atomistic simulation perspective, an affirmative answer to this question implies that, if we can characterize the configuration space accessible at a temperature $T$—as can be done, e.g., with Monte Carlo (MC) methods—we can also calculate any quantity of interest. In particular, time-correlation functions would become available, which would allow us to compute nontrivial properties like $T$-dependent phonon spectra or lattice thermal-transport coefficients without explicitly solving the equations of motion. Such a *nondynamical* approach would have many advantages: As in MC schemes, fixing $T$ would become trivial, and we would avoid the problems associated with the use of thermostats in molecular-dynamics (MD) simulations; there would be no need for very long MD runs to access low-frequency phenomena, etc.

In the particular case of the vibrational spectrum, several heuristic schemes have been proposed to realize such a goal. For example, Hellman *et al.* [1] compute phonons at finite $T$ from an *effective* dynamical matrix that they postulate and obtain in a computationally efficient way. A similar effective potential is used in Refs. [2,3] to capture anharmonic effects in the vibrational spectrum; others have used the harmonic relation between a normal-mode frequency and the amplitude of its oscillations to compute dynamical properties even from powder diffraction data [4–6]. While such methods are valuable, we have to resort to earlier works to find a rigorous and general treatment. As recognized in a variety of fields [7–9], a time-correlation function can be obtained from the knowledge of its moments, which are *static* quantities that can be computed from efficient statistical simulations. In the context of lattice-dynamical studies, the moment-based approach introduced by Mori [9,10] has been used to investigate a number of simple systems at both the quantum and classical levels [10–14]; however, it has failed to gain popularity in the field of classical MD. As far as we can see, this is probably because (1) we lack a general scheme to tackle arbitrarily complex materials with many atoms in the cell and (2) there has not been enough work to identify the simplest approximations that may render useful results (i.e., reliable phonon frequencies and possibly peak widths). Here we present our own derivation of a moment-based formalism for the classical case, remedying the mentioned deficiencies. The resulting theory allows us to clarify the status of the heuristic methods in the literature and, in our opinion, should become a standard tool in the field of classical simulations.

*General formalism.*—We define the classical correlation function of quantities $A_i$ and $B_j$ as

$$C_{ij}^{AB}(t) = \langle A_i(0)B_j(t)\rangle = \int_{-\infty}^{\infty} C_{ij}^{AB}(\omega)e^{i\omega t}d\omega, \quad (1)$$

where the angled brackets indicate thermal averaging and $C_{ij}^{AB}(\omega)$ is the corresponding *spectral function*. Below, we will identify $A_i$ and $B_j$ with atomic positions or velocities, $i$ and $j$ being composite indices that label an atom and a direction in space. Note that $C_{ij}^{AB}(t)$ is real, which implies $C_{ij}^{AB}(-\omega) = [C_{ij}^{AB}(\omega)]^*$. For simplicity, we will work with the real part $\tilde{C}_{ij}^{AA}(\omega) = \Re[C_{ij}^{AA}(\omega)]$, as this will contain the information about the vibrational spectrum [15]. Thus, in the time domain, we have

$$\tilde{C}_{ij}^{AA}(t) = \int_{-\infty}^{\infty} \tilde{C}_{ij}^{AA}(\omega)\cos(\omega t)d\omega, \quad (2)$$

which is even with respect to time inversion and can be Taylor expanded in the following way:

$$\tilde{C}_{ij}^{AA}(t) = \sum_{n=0}^{\infty}(-1)^n \frac{\mu_{ij}^{A,2n}}{(2n!)} t^{2n}, \quad (3)$$

with the moments given by

$$\mu_{ij}^{A,2n} = \int_{-\infty}^{\infty} \omega^{2n}\tilde{C}_{ij}^{AA}(\omega)d\omega. \quad (4)$$

The next key step is to prove that these moments can be written as certain correlation functions at $t = 0$ and can thus be computed as regular thermal averages. By successive partial integration, one can see that

$$\tilde{C}_{ij}^{AA}(\omega) = \omega^{-2}\tilde{C}_{ij}^{A^{(1)}A^{(1)}}(\omega) = -\omega^{-2}\tilde{C}_{ij}^{A^{(2)}A}(\omega) = \frac{(-1)^{m+n}}{\omega^{2m+2n+2p}}\tilde{C}_{ij}^{A^{(2m+p)}A^{(2n+p)}}(\omega), \tag{5}$$

where $A_i^{(n)}$ is the $n$th time derivative of $A_i$. These identities allow us to rewrite Eq. (4) in different ways. From a computational viewpoint, it is convenient to use

$$\mu_{ij}^{A,2n} = \int_{-\infty}^{\infty}\tilde{C}_{ij}^{A^{(n)}A^{(n)}}(\omega)d\omega = \langle A_i^{(n)}(0)A_j^{(n)}(0)\rangle, \tag{6}$$

which involves time derivatives of the lowest possible order. Finally, the derivatives can be computed using Hamilton's equation of motion

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A, H\},$$
$$\{A, H\} = \sum_i\left(\frac{\partial A}{\partial x_i}\frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial H}{\partial x_i}\right). \tag{7}$$

The Hamiltonian is

$$H = \sum_i \frac{p_i^2}{2m_i} + V(\{x_i\}), \tag{8}$$

where $m_i$, $x_i$, and $p_i$ are mass, position, and momentum, respectively, and $V$ is a velocity-independent potential. It is convenient to introduce $x_i' = \sqrt{m_i}x_i$ to get rid of the mass dependence in the kinetic energy. We will thus work with the moments $\mu_{ij}^{A',2n}$ of the correlation function $\tilde{C}_{ij}^{A'A'}(t) = \sqrt{m_im_j}\tilde{C}_{ij}^{AA}(t)$, where $A_i' = \sqrt{m_i}A_i$. The simplest object that gives information about the vibrational spectrum is the position-position correlation function. By taking $A_i' = \bar{x}_i' = x_i' - \langle x_i'\rangle$, we obtain

$$\mu_{ij}^{\bar{x}',0} = \sqrt{m_im_j}(\langle x_ix_j\rangle - \langle x_i\rangle\langle x_j\rangle),$$
$$\mu_{ij}^{\bar{x}',2} = \beta^{-1}\delta_{ij},$$
$$\mu_{ij}^{\bar{x}',4} = \frac{1}{\sqrt{m_im_j}}\left\langle\frac{\partial V}{\partial x_i}\frac{\partial V}{\partial x_j}\right\rangle,$$
$$\mu_{ij}^{\bar{x}',6} = \frac{\beta^{-1}}{\sqrt{m_im_j}}\sum_k\frac{1}{m_k}\left\langle\frac{\partial^2 V}{\partial x_i\partial x_k}\frac{\partial^2 V}{\partial x_k\partial x_j}\right\rangle \tag{9}$$

for the four lowest moments of Eq. (3). Here, we reversed the mass scaling at the last step of the derivation, so as to express the moments in terms of the regular atomic positions. We also used $\langle p_i'p_j'\rangle = k_BT\delta_{ij} = \beta^{-1}\delta_{ij}$ and $\langle f(\{p_i'\})g(\{x_i'\})\rangle = \langle f(\{p_i'\})\rangle\langle g(\{x_i'\})\rangle$, where $f$ and $g$ are arbitrary functions. Let us stress that this procedure renders $\mu_{ij}^{\bar{x}',2}$ proportional to the identity matrix, a fact that will be advantageous later. As an example of the freedom we have in writing the moments, note that alternatively we can get

$$\mu_{ij}^{\bar{x}',4} = -\langle x_i'^{(3)}x_j'^{(1)}\rangle = \frac{\beta^{-1}}{\sqrt{m_im_j}}\left\langle\frac{\partial^2 V}{\partial x_i\partial x_j}\right\rangle. \tag{10}$$

It is also interesting to note that other time-correlation functions can be readily computed from Eq. (9). Indeed, it can be seen from Eqs. (4) and (5) that

$$\mu_{ij}^{A^{(1)},2n} = \mu_{ij}^{A,2n+2}. \tag{11}$$

Thus, for example, the lowest nondiagonal moment of the velocity-velocity correlation function is $\mu_{ij}^{v',2} = \mu_{ij}^{\bar{x}',4}$.

In order to gain physical insight, consider the case of a single harmonic oscillator. There, we know the exact form of $C^{\bar{x}'\bar{x}'}(\omega) = \mu^{\bar{x}',0}[\delta(\omega-\omega_0) + \delta(\omega+\omega_0)]/2$, and from Eqs. (4) and (9) we obtain $\omega_0^{2n} = \mu^{\bar{x}',2n}/\mu^{\bar{x}',0}$; then, for $n = 1$, we have $m\omega_0^2 = [\beta(\langle x^2\rangle - \langle x\rangle^2)]^{-1}$. We thus find that the fluctuations of the position give us the frequency of the (phonon) peak in the $C^{\bar{x}'\bar{x}'}(\omega)$ spectrum. (This is essentially the quasiharmonic result used in Refs. [4,6].) Similarly, for $C^{v'v'}(\omega)$, we get $m\omega_0^2 = \langle\partial^2V/\partial x^2\rangle$; i.e., the frequency is given by the thermal-averaged dynamical matrix in this case. These intuitive relations, which are exact in the harmonic limit and are generalized below to the many-body case, are implicitly underlying the heuristic methods to estimate the phonon frequencies mentioned above [1–3].

*Practical scheme.*—In general, we will have many interacting atoms and an anharmonic potential $V$. To simplify the problem, let us make a unitary coordinate transformation $A_a' = \sum_i T_{ai}^*A_i'$ that will be analogous to the usual change into a normal-mode basis. We write the transformed correlation function and moments as

$$\tilde{C}_{ab}^{A'A'}(t) = \sum_{ij}T_{ai}^*\tilde{C}_{ij}^{A'A'}(t)T_{bj}, \tag{12}$$

$$\mu_{ab}^{A',2n} = \sum_{ij}T_{ai}^*\mu_{ij}^{A',2n}T_{bj}. \tag{13}$$

We choose $T_{ai}$ to diagonalize the lowest nondiagonal moment $\check{\mu}_{ij}^{A'}$, so that

$$\sum_{ij}T_{ai}^*\check{\mu}_{ij}^{A'}T_{bj} = \check{\mu}_a^{A'}\delta_{ab}. \tag{14}$$

Note that $T_{ai}$ gives the *polarization vectors* of our normal modes. We then approximate [16]

$$\tilde{C}_{ij}^{A'A'}(t) = \sum_{ab}T_{ia}^*\tilde{C}_{ab}^{A'A'}(t)T_{jb} \approx \sum_a T_{ia}^*C_{aa}^{A'A'}(t)T_{ja}, \tag{15}$$

where the second equality is exact to low order in the moment expansion. Hence, to investigate the spectrum given by $\tilde{C}_{ij}^{A'A'}(\omega)$, we will work with the collection of anharmonic oscillators $C_{aa}^{A'A'}(\omega)$ [16].

Now, we have $\check{\mu}_{ij}^{\bar{x}'} = \mu_{ij}^{\bar{x}',0}$ and $\check{\mu}_{ij}^{v'} = \mu_{ij}^{v',2}$. Interestingly, thanks to the mass-scaling transformation, $\mu_{ij}^{\bar{x}',2}$ and $\mu_{ij}^{v',0}$ are proportional to the identity matrix and will remain diagonal in our normal-mode basis. Thus, since the two lowest-order moments are diagonal for both $\tilde{C}_{ab}^{\bar{x}'\bar{x}'}$ and $\tilde{C}_{ab}^{v'v'}$, it seems reasonable to propose the following *effective-harmonic approximation*

$$C_{aa}^{A'A'}(t) = \mu_{aa}^{A',0}\left(1 - \frac{1}{2}\frac{\mu_{aa}^{A',2}}{\mu_{aa}^{A',0}}t^2 + \cdots\right) \approx \mu_{aa}^{A',0}\cos(\omega_a t), \tag{16}$$

where $\omega_a = \sqrt{\mu_{aa}^{A',2}/\mu_{aa}^{A',0}}$.

For $A'_i = \bar{x}'_i$, Eq. (14) involves the diagonalization of $\mu_{ij}^{\bar{x}',0} = \sqrt{m_i m_j}(\langle x_i x_j\rangle - \langle x_i\rangle\langle x_j\rangle)$; for $A'_i = v'_i$, we diagonalize $\mu_{ij}^{v',2} = \mu_{ij}^{\bar{x}',4}$, which can be expressed as the thermal-averaged dynamical matrix of Eq. (10). Hence, the eigenvalues of these matrices provide us with a rigorously justified approximation to the position of the (phonon) peaks in the $C_{aa}^{A'A'}(\omega)$ spectra; as described above, they render the exact phonon frequencies in the harmonic limit.

In order to capture more complex line shapes, we need a strategy to treat the full $C_{aa}^{A'A'}(\omega)$. One possibility is to assume an analytic form for it, with free parameters that can typically be written as a function of the low-order moments. We worked with some physically motivated choices, i.e., Gaussians, Lorentzians, and combinations of delta functions. Such an approach allowed us to compute the peak frequencies for a variety of model systems, even in the presence of significant nonlinear effects (i.e., overtones). However, the scheme failed to provide a quantitative estimate of the peak widths; further, for models with very strongly $T$-dependent frequencies, we sometimes obtained nonphysical solutions for the parameters of the trial spectral functions.

Fortunately, we found it possible to treat $C_{aa}^{A'A'}(\omega)$ in a robust and accurate way by resorting to Mori's continued-fraction representation [9]. Using the notation of Ref. [11], we write for a generic, real autocorrelation function $C(\omega)$

$$C(\omega) = \frac{\mu^0}{\pi}\Re[\psi_0(i\omega)], \qquad \psi_n(z) = \frac{1}{z + \delta_{n+1}\psi_{n+1}(z)}, \tag{17}$$

where the $\delta_n$ parameters are explicit functions of the moments. The first three are given by [11]

$$\delta_1 = \frac{\mu^2}{\mu^0}, \qquad \delta_2 = \frac{\mu^4}{\mu^2} - \frac{\mu^2}{\mu^0}, \qquad \delta_3 = \frac{1}{\delta_2}\left\{\frac{\mu^6}{\mu^2} - \left[\frac{\mu^4}{\mu^2}\right]^2\right\}. \tag{18}$$

A continued fraction is usually terminated by assuming the last $\psi_n(z)$ term to be the Laplace transform of some model function. Many terminations have been used in the literature [10–14]; yet, we found that, for the model systems we investigated, the line shape is quite insensitive to the termination scheme when including up to sixth moments; thus, we simply used for $\psi_2(z)$ the Gaussian termination described in Ref. [11]. Obviously, in this scheme, a separate continued-fraction expansion must be calculated for each $C_{aa}^{A'A'}(\omega)$. In practice, we first compute the *atomic* moments $\mu_{ij}^{A',2n}$ and then obtain those corresponding to our normal modes by using Eq. (13).

*Example of application.*—To test our approach, we used it to compute vibrational spectra—with moments calculated from MC simulations—and compared the results with the exact ones obtained from MD [17,18]. We worked with model systems, which gave us full control of the potential-energy surface and allowed us to try the method in very diverse and challenging situations. Overall, we found that our approach renders excellent results for the main features of the vibrational spectrum. To illustrate the method, here we describe a particularly demanding case, namely, a system undergoing a structural phase transition driven by a soft phonon mode.

Let us consider a cubic crystal with 3 degrees of freedom $x_{l\alpha}$ per cell $l$, where $\alpha = x$, $y$, and $z$. For simplicity, we take $m = 1$ and write the Hamiltonian as

$$\begin{aligned} H = {} & \frac{1}{2}\sum_{l\alpha} p_{l\alpha}^2 + c_1\sum_l (|\vec{x}_l|^2 - 1)^2 \\ & + c_2\sum_l (x_{lx}^2 x_{ly}^2 + x_{ly}^2 x_{lz}^2 + x_{lz}^2 x_{lx}^2) \\ & + \frac{1}{2}{\sum_{ll'}}' \Big[ c_3|\vec{x}_l - \vec{x}_{l'}|^2 + c_4|x_{l\alpha(ll')} - x_{l'\alpha(ll')}|^2 \Big], \end{aligned} \tag{19}$$

where the primed sum is restricted to nearest-neighboring cells and $\alpha(ll')$ is given by the direction of the lattice vector connecting cells $l$ and $l'$. In essence, this is the well-known discrete $\phi^4$ model [19–21], extended to include (1) an on-site anisotropic term ($c_2 > 0$) chosen so that the ground state has a tetragonal symmetry and (2) a coupling between nearest neighbors ($c_4$) that breaks the symmetry between longitudinal and transversal phonon branches. Here, we show representative results obtained for a choice of parameters ($c_1 = 0.25$, $c_2 = 0.50$, $c_3 = 1.00$, and $c_4 = 0.50$) that leads to a second-order displacive [22] phase transition. While the energy units are arbitrary, this model renders a realistic representation of a phase transition at room temperature.

We simulated the model in a periodically repeated 20 × 20 × 20 supercell. We carefully checked the convergence of the MC and MD simulations. For example, the MD results shown here were obtained by Fourier transforming time-correlation functions computed from constant-energy trajectories whose starting points were snapshots taken from a constant-$T$ Langevin simulation. For each $T$ investigated, ten different starting points were considered, the final spectral function being an average.

In periodic systems, the moments, as well as the time-correlation and spectral functions, become block diagonal in the Bloch representation. Hence, instead of the $\tilde{C}_{ij}^{A'A'}$ and

$C^{A'A'}_{aa}$ functions in the formulas above, in the following, we will use the Fourier-transformed $\tilde{C}^{A'A'}_{\mathbf{q},\alpha\beta}$ and $C^{A'A'}_{\mathbf{q},aa}$, where $\mathbf{q}$ is a vector in the first Brillouin zone of our model crystal; the corresponding moments are $\mu^{A',2n}_{\mathbf{q},\alpha\beta}$, etc.

Figures 1(a) and 1(b) show the phonon bands at low and high $T$'s, respectively. The MD results were obtained from the first moment of the peaks in the spectrum given by the trace of $\tilde{C}^{v'v'}_{\mathbf{q},\alpha\beta}(\omega)$. The MC results were obtained by diagonalizing $\mu^{v',2}_{\mathbf{q},\alpha\beta}$ within our effective-harmonic approximation [Eq. (16)]. The agreement is excellent.

Figure 1(c) shows the $T$-dependent frequencies of the phonons at the $\Gamma$ point ($\mathbf{q} = 0$). In the cubic phase, the frequencies decrease as $T$ is reduced and essentially vanish at the critical temperature $T_C$. Then, below $T_C$, the frequencies increase as $T$ decreases. We have three $\Gamma$ phonons in both phases: They are threefold degenerate in the cubic structure but split in two groups when the symmetry is lowered to tetragonal. In the figure, we show the trace of the $\tilde{C}^{\bar{x}'\bar{x}'}_{\Gamma,\alpha\beta}(\omega)$ functions resulting from MD simulations, as well as the frequencies computed at the effective-harmonic level by diagonalizing $\mu^{\bar{x}',0}_{\Gamma,\alpha\beta}$ obtained from MC calculations. This approximation gives excellent results, even in the immediate vicinity of $T_C$ where the system is strongly anharmonic.

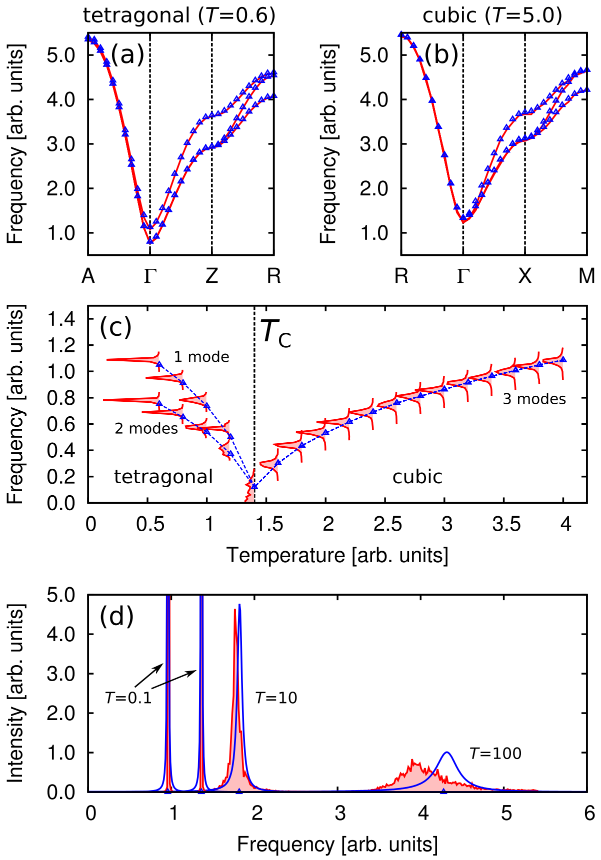

FIG. 1 (color online). Dynamical properties of our model system. We show the results obtained from our approach based on MC simulations (blue symbols and lines) and the *exact* MD results (red lines). (a), (b) Phonon bands at two different $T$'s. (c) Spectrum at the $\Gamma$ point for $T$'s around the critical temperature $T_C$. (d) $\Gamma$ spectrum at selected $T$'s. All spectra are normalized to unity. See the text for more details.

Figure 1(d) shows the line shapes from the continued-fraction representation of $C^{\bar{x}'\bar{x}'}_{\Gamma,aa}(\omega)$, using up to the sixth-order moments, together with the MD results. We can appreciate that the widths of the peaks obtained with our method are semiquantiatively correct. We include a result at an unrealistically high $T = 100$, where the peak broadening is very significant. Even in such extreme conditions, our approximate spectral function provides a fair representation of the exact one.

*Final remarks.*—We have shown that the main features of classical vibrational spectra can be accurately computed from knowledge of the low-order moments of the appropriate time-correlation functions. More precisely, we have presented a way to compute a normal-mode-like basis that renders the low-order moments diagonal, which allows us to approximate the full spectrum by a collection of anharmonic oscillators [Eq. (15)]. Further, we have introduced an effective-harmonic approximation [Eq. (16)] that makes it possible to obtain very accurate results for the vibrational frequencies from simple statistical averages of atomic positions or forces. We have also shown that it is possible to reproduce the line shape of the spectral functions in a semiquantitative way, provided that higher moments are available.

The moments can be obtained as thermal averages from MC simulations. Alternatively, one may obtain them from MD simulations, without the need to explicitly compute the time-correlation functions; this should allow for shorter MD runs (only as long as needed to compute accurate thermal averages) and to simplify the use of thermostats (as their interfering with the dynamics would be unimportant).

Our effective-harmonic treatment provides a rigorous justification for some of the assumptions underlying previous schemes in the literature [1–3]. Further, first-principles methods like the one proposed in Ref. [1] could greatly benefit from results such as the identity $\langle \partial^2 V/\partial x_i \partial x_j \rangle = \beta \langle (\partial V/\partial x_i)(\partial V/\partial x_j) \rangle$, which we have proven here and constitutes a convenient way to obtain the thermal-averaged force-constant matrix (computationally very costly) from appropriate products of forces (readily available). Finally, our effective-harmonic approximation can be connected with quasiharmonic methods that have been applied in a variety of contexts [4–6]; our results support the applicability of such schemes even in cases with significant anharmonicity.

We hope the methods here discussed will become standard tools in classical simulations, where they can be used to a great advantage.

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