Atomistic Framework for Time-Dependent Thermal Transport

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ABSTRACT: Phonons play a major role for the performance of nanoscale devices and consequently a detailed understanding of phonon dynamics is required. Using an auxiliary-mode approach, which has successfully been applied for the case of electrons, we develop a new method to numerically describe time-dependent phonon transport. This method allows one to gain insight into the behavior of local vibrations in molecular junctions, which are driven by time-dependent temperature differences between thermal baths. Exemplarily, we apply the method to study the nonequilibrium dynamics of quantum heat transport in an one-dimensional atomic chain as well as in realistic molecular junctions made of polyacetylene and polyethylene chains, in which the vibrational structure of the junction is described at the density functional theory level. We calculate the transient energies and heat currents and compare the latter to the standard Landauer approach in thermal equilibrium. We show that the auxiliary-mode representation is a powerful and versatile tool to study time-dependent thermal transport in nanoscale systems.

INTRODUCTION

The feasibility of nanoscale functional devices depends crucially on the ability to control the relevant microscopic degrees of freedom: electrons for nanoelectronics,1,2 spins in spintronics3,4 and phonons in nanophononics5,6. Although many problems belonging to the former two fields have already been in the focus of intensive experimental and theoretical efforts for a long time, the issue of tuning thermal transport by influencing vibrational degrees of freedom in nanophononic devices is a relatively new field.7−10 So far, the majority of theoretical studies of quantum phonon transport in nanoscale systems deals with stationary situations within the harmonic approximation. Here, the Landauer approach, based on the calculation of transmission functions, can be used.11−14 To include the anharmonic contributions, one needs to resort to full nonequilibrium Green’s function (NEGF) schemes.15−18 Both methodologies can eventually be combined with density functional-based modeling to achieve an atomistic level of description.18−24

In nonstationary situations, where time-dependent (TD) external parameters can strongly affect a nanoscale system, the dynamics of the vibrational system becomes crucial. For example, a time-varying temperature bias25−30 or strong local heating by laser fields28−30 can be used to exert additional control over thermal transport. In this context, novel nonequilibrium effects, like molecular heat pumping31,32 cooling33 and rectification,34−36 have been proposed. The description of such phenomena often requires working directly in the time domain, which is very challenging from a numerical point of view. In this respect, considerable progress has been achieved in the description of TD transport of spins37−39 and electrons40−53. However, less attention has been paid to a similar treatment of vibrational degrees of freedom. Thus, only recently new approaches have been developed to deal with TD thermal phenomena in nanojunctions34−56. Yet, the application of those approaches is mostly limited to simple model systems, so that the issue of combining the time-dependent approach with an atomistic material description remains open and very challenging.

In this article, we present a novel atomistic method capable of studying time-dependent phonon transport in nanosystems by combining a TD-NEGF approach with density functional theory-based modeling. This computational method is based on the solution of the equation of motion (EOM) of the phonon density matrix by developing an auxiliary-mode approach. This very efficient scheme has already been successfully used for various investigations of time-resolved electron transport.51−56 As we show, the efficiency of the auxiliary-mode scheme can be used to study phonon transport in open nanoscale systems. As a proof-of-principle, we first

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consider an one-dimensional (1D) atomic chain and in a second step carbon-based molecular junctions to demonstrate the potential of the method to describe time-dependent transport in realistic nanoscale materials.

■ MODEL AND COMPUTATIONAL METHOD

The basic setup of our approach is shown in Figure 1. Two thermal baths consisting of noninteracting harmonic oscillators are connected to a generic scattering region, whose vibrational properties are assumed to be well represented by a purely harmonic Hamilton operator. The total system is then described by the following Hamiltonian

\[
H = H_C + \sum_{ak} \left( \frac{1}{2} p_{ak}^2 + \frac{1}{2} \omega_{ak}^2 u_{ak}^2 \right) + \sum_{\alpha,k} \left( \frac{1}{2} (u^T V_{ak} u_{ak} + u_{ak} V_{ak}^T u) \right)
\]

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The first term \( H_C \) is \( (1/2)p^T \cdot p + (1/2)u^T \cdot K_{eff} \cdot u \) is the Hamiltonian of the central region, \( u \) is a column vector consisting of all of the atomic displacement variables in the region, and \( p \) contains the corresponding momenta. Both vectors have length \( N \), where \( N \) is the number of vibrational degrees of freedom in the central region. We have chosen renormalized displacements \( u_i = \sqrt{m_i} \xi_i \), where \( m_i \) is the mass associated with the \( i \)th vibrational degree of freedom and \( \xi_i \) is the actual displacement having the dimension of length. The effective force-constant matrix \( K_{eff} = K + K_C \) has dimension \( N \times N \) and includes the force-constant matrix of the central region, \( K_C \), as well as a counter-term \( K_{eff} \), which is provided in the Supporting Information.

The second term of eq 1 is the Hamiltonian of the heat bath. The last term represents the interaction between the central region and the baths, which is given by coupling vectors \( V_{ak} \) that are assumed to vanish before time \( t_0 \). Written in this form, the coupling leads to a renormalization of the bare dynamical matrix, which can be canceled by the previously mentioned counter-term \( K_{eff} = \sum_{ak} (V_{ak} V_{ak}^T) / \omega_{ak}^2 \). Consequently, the coupling to the thermal baths will solely introduce dissipation rather than a shift in the vibrational spectrum of the system.

The energy of the central region, \( E_C(t) \), can be expressed in terms of the phonon density matrix \( \sigma(t) = i \mathcal{G}^\uparrow(t, t') \), where \( \mathcal{G}^\uparrow(t, t') \) is the lesser Green function (GF), as

\[
E_C(t) = (1/2) \text{Tr} \{ \mathcal{K}_{eff}^T \mathcal{Q} \sigma(t) \}. 
\]

Here and in the following, we adopt units with \( \hbar = 1 \). Moreover, we have introduced the \( 2N \times 2N \) dimensional auxiliary matrices (we use caligraphic symbols to denote matrices with dimension \( 2N \times 2N \) throughout the manuscript)

\[
I \equiv \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad Q \equiv \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}, \quad \mathcal{K}_{eff} \equiv \begin{bmatrix} 0 & 1 \\ -\mathcal{K}_{eff} & 0 \end{bmatrix}
\]

If no external force is acting on the system, the total energy must be conserved, and the heat current coming from both heat baths can be defined as \( J(t) = -\frac{\partial E_C(t)}{\partial t} \). Therefore, the time evolution of the heat current is related to the lesser GF, which can be written as a \( 2N \times 2N \) block matrix

\[
\mathcal{G}^\uparrow(t, t') = -i \begin{bmatrix} \langle u(t')^T u^T(t) \rangle & \langle u(t')^T p^T(t) \rangle \\ \langle p(t')^T u(t) \rangle & \langle p(t')^T p^T(t) \rangle \end{bmatrix}
\]

Note that the GF includes displacement \( u \) and momentum \( p \) vectors on the same footing. By using the Hamiltonian given by eq 1 and the GF relations given in the Supporting Information (see eqs S1–S3), we find that the density matrix satisfies the following equation of motion (EOM)

\[
\frac{\partial}{\partial t} \sigma(t) = \mathcal{K}_{eff}^T \sigma(t) + \sigma(t) \mathcal{K}_{eff}^T + i \sum_{\alpha} \left[ \left[ \Pi_{\alpha} \mathcal{Q}^T + h. c. \right] \right]
\]

Here, we have defined the phonon current matrices \( \Pi_{\alpha}(t) \) as

\[
\Pi_{\alpha}(t) = \int_{t_0}^t dt' \langle \mathcal{G}^\uparrow(t', t') S_{\alpha^\uparrow}(t', t) - \mathcal{G}^\uparrow(t, t') S_{\alpha^\uparrow}(t, t') \rangle
\]

Consequently, the heat current from reservoir \( \alpha \) into the system can be conveniently expressed in terms of \( \Pi_{\alpha} \) as

\[
J_{\alpha}(t) = -\frac{i}{2} \text{Tr} \left\{ \mathcal{K}_{eff}^T \mathcal{Q} \left[ \Pi_{\alpha}(t) \mathcal{Q}^T + h. c. \right] \right\}
\]

The current matrices contain memory effects through the self-energies \( S_{\alpha^\uparrow} \). Since the thermal baths are harmonic, the self-energies \( S_{\alpha^\uparrow}(t, t') \) can be explicitly calculated

\[
S_{\alpha^\uparrow}(t, t') = -i \int_0^\infty \frac{d\omega}{\pi} \left[ \coth \frac{\omega}{2k_B T_a} \cos \omega(t - t') \pm i \sin \omega(t - t') \right] \mathcal{L}_a(\omega)
\]

Here, \( T_a \) is the bath temperature and \( \mathcal{L}_a(\omega) \) is the bath spectral density of reservoir \( \alpha \), which characterizes the action of the environment on the open system. Together, a complicated set of coupled integro-differential equations for realistic systems is obtained (eqs 3 and 4). To proceed further, we use an auxiliary-mode representation of the self-energies in terms of exponential functions, which has previously been developed for electrons\(^{41,46}\) and for vibrations\(^{59,61}\) (details are provided in the Supporting Information). The bath spectral density is given by the specific form of the coupling to the heat reservoirs and can be computed using a recursive GF scheme.\(^{57,59}\) Following the auxiliary-mode approach, we consider a spectral density with a Drude regularization (i.e., adding a cut-off frequency \( \omega_c \)) of the form

\[
\mathcal{L}_a(\omega) = (\omega^2_c + i \omega_c) \mathcal{L}_a^0. \quad \text{Here,} \quad \mathcal{L}_a^0 \equiv \text{diag}(\Lambda_a^0, 0)
\]

contains the coupling strength matrix \( \Lambda_a^0 \) of the central region to the leads (see Section 2 in the
Supporting Information for details). This spectral density contains the wide-band limit as a special case for \( \omega_i \rightarrow \infty \). Moreover, using a linear combination of several Lorentzians, any spectral density can in principle be approximated. In this way, the self-energies can be written as

\[
S_{\alpha \beta}^<(t, t') = \sum_{\nu} S_{\alpha \beta}^{\nu}(0) \mathcal{L}^0_{\nu}(0) e^{-\omega_{\nu} |t - t'|} \mathcal{L}^0_{\nu}(0),
\]

where the coefficients \( a_{\alpha \beta}^{\nu} \) and \( b_{\alpha \beta}^{\nu} \) are related to the auxiliary-mode decomposition (see eqs S10 and S11 in the Supporting Information). The phonon current matrices \( \Pi_{\alpha}(t) \) can then be expressed as

\[
\Pi_{\alpha}(t) = \sum_{\nu=0}^{N_{\Pi}} \left[ \Phi_{\alpha}^{\nu}(t) + a_{\alpha \beta}^{\nu} Q \mathcal{L}^0_{\nu}(0) \right]
\]

where \( N_{\Pi} \) is the number of poles used in the auxiliary-mode expansion. The functions \( \Phi_{\alpha}^{\nu}(t) \) (see eq S13 in the Supporting Information) are also obtained through the solution of their EOMs

\[
\frac{\partial}{\partial t} \Phi_{\alpha}^{\nu}(t) = \mathcal{A}_{\alpha}^{\nu} \Phi_{\alpha}^{\nu}(t) - \mathcal{B}_{\alpha}^{\nu} \mathcal{K}^T \mathcal{L}^0_{\nu}(0) + Q \mathcal{L}^0_{\nu}(t)
\]

(7)

where \( \mathcal{A}_{\alpha}^{\nu} = K - b_{\alpha \beta}^{\nu} T \) and \( \mathcal{B}_{\alpha}^{\nu} = i \omega_{\nu} \delta_{\alpha \beta} \sigma(t) + a_{\alpha \beta}^{\nu} Q \). The functions \( Q \mathcal{L}^0_{\nu}(t) = \sum_{\nu=0}^{N_{\Pi}} \mathcal{L}^0_{\nu}(0) \mathcal{L}^0_{\nu}(t) \) correlate the main features of both heat baths, and their values are obtained by performing the time derivative of \( \Omega_{\alpha}^{\nu}(t) \)

\[
\frac{\partial}{\partial t} \Omega_{\alpha}^{\nu}(t) = C_{\alpha}^{\nu} \mathcal{L}^0_{\nu}(0) Q \mathcal{K}^T \mathcal{L}^0_{\nu}(0) - D_{\alpha}^{\nu} \Omega_{\alpha}^{\nu}(t) - \omega_{\nu} \delta_{\alpha \beta} \mathcal{K} \mathcal{L}^0_{\nu}(0) - \delta_{\alpha \beta} \mathcal{L}^0_{\nu}(t)
\]

(8)

\( C_{\alpha}^{\nu} = a_{\alpha \beta}^{\nu} a_{\alpha \beta}^{\nu} - a_{\alpha \beta}^{\nu} a_{\alpha \beta}^{\nu} \) and \( D_{\alpha}^{\nu} = b_{\alpha \beta}^{\nu} + b_{\alpha \beta}^{\nu} \) are real numbers. Thus, the original integro-differential equation for the reduced density matrix is mapped onto a closed set of ordinary differential equations (eqs 3, 7, and 8), which are solved in this study by the fourth-order Runge-Kutta method with a timestep of 0.1 fs.

### RESULTS AND DISCUSSION

#### One-Dimensional Chain.

To illustrate this general method, we first consider, for the central region, an one-dimensional (1D) linear chain consisting of \( N \) atoms coupled by force constants with magnitude \( \lambda = 1.0 \text{ eV/Å}^2 \). In this case, the coupling matrix to the reservoirs has only one nonzero entry \( \eta \), which characterizes the coupling strength, i.e., \( (\Lambda_{\alpha}^{0})_{NN} = \eta \) and \( (\Lambda_{\alpha}^{0})_{11} = \eta \). After extensive benchmarking of the parameters related to the Drude spectral density (see Section 2 in the Supporting Information), we have chosen the coupling parameters \( \eta = \lambda/2 \) and \( \omega_{\nu} = 1000 \text{ THz} \) for both baths. These parameters provide an accurate description of the phonon spectrum in this 1D model, and the heat current values in the steady state are in good agreement with those obtained by the Landauer approach, as shown below.

In Figure 2, we show the total energy after thermal equilibration \( (T_0 = T_l = T_R) \) as a function of the number of poles used in the auxiliary-mode expansion for the case of a dimer \( (N = 2) \). Although the heat current tends to 0 for each \( N_p \) (see the inset in Figure 2), the system energy in the steady state still grows as \( N_p \) increases. It converges for a given \( N_p \) value depending on the temperature, e.g., 16 and 8 poles are needed to reach convergence at 50 and 300 K, respectively.

This is related to the fact that only few poles are sufficient to describe high-temperature effects in the auxiliary-mode approach.\(^{59}\) The final energy values are close to those obtained for an ideal harmonic oscillator in thermal equilibrium, \( E_C = \sum_{\nu} n(\omega_{\nu}) + 1/2 \), where \( n(\omega_{\nu}) \) is the Bose-Einstein distribution function and \( \omega_{\nu} \) are the frequencies of the isolated central system. Thus, we expect to find \( E_C = 8.83 \times 10^{-2} \) and \( 9.56 \times 10^{-2} \) eV at 50 and 300 K, respectively. The discrepancies observed in Figure 2 relate to the coupling to the baths, i.e., they vanish in the weak coupling limit \( \eta \rightarrow 0 \), as it is shown in Figure S1 of the Supporting Information.

To gain further insight, we perform an eigenvalue decomposition of the quantity \( \mathcal{Z}(t) = (1/2) \mathcal{K}^T \mathcal{L}^0(t) \), which is related to the total energy of the central region after tracing out the bath degrees of freedom. To this end, we solve the eigenvalue problem for the \( N \times N \) matrix resulting from adding the diagonal blocks of \( \mathcal{Z}(t) \). In Figure 3a, we present the time evolution of the two eigenvalues for the diatomic chain at \( T_0 = 300 \text{ K} \). Both eigenvalues increase as a function of time and reach their time-independent limit once the system reaches equilibrium. Moreover, by analyzing the corresponding eigenvectors, one finds that the lower mode \( (E_1) \) corresponds to the case when the atoms vibrate with the same amplitude and in-phase (acoustic-like mode). This mode corresponds to the zero frequency translational mode of the isolated dimer; since translational symmetry is now broken due to the coupling to the baths, the mode acquires a finite frequency. The other mode \( (E_2) \) corresponds to the stretching mode of the dimer, where the atoms vibrate out of phase.

Once the system has reached thermal equilibrium at time \( t_s \), we apply a symmetric temperature bias \( \Delta T = T_0 - T_R = 2 \xi T_0 \) \((\xi > 0)\) with \( T_0 \) corresponding to the mean temperature at which the system was previously equilibrated. The temperatures for the left and right leads can be written as \( T_l = (1 + \xi) T_0 \) and \( T_R = (1 - \xi) T_0 \) respectively. Here, we define \( t = t - t_s \) as the simulation time after the temperature bias is switched on. In the insets of Figure 3a, we show the time evolution of the eigenvalues associated to the acoustic and optical modes of the diatomic chain for two different values of the temperature bias, \( \Delta T = 60 \) and 180 K. As \( \Delta T \) increases, the fluctuations during the transient get larger because the central region exchanges a larger amount of energy with the heat baths in order to stabilize the entire system. As a function of time, the energy \( E_1 \) first decreases and then increases until reaching the

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**Figure 2.** Energy of a diatomic chain vs number of poles \( N_p \) of the auxiliary-mode approach at different temperatures. The arrows indicate the convergence point for each temperature. Inset: dynamics of the heat current for the diatomic chain at \( T_0 = 50 \text{ K} \).
steady state, whereas the optical mode $E_2$ is strongly affected during the transient, and it displays larger fluctuations than $E_1$. The time evolution of the heat current in both leads for linear chains containing two and eight atoms is presented in Figure 3b. In both cases, the transients show similar features: the heat current grows, oscillates and then saturates. One can also see that the time for reaching the steady state is longer for larger systems. The heat current in the steady state for several chain sizes at 300 K and for different values of the temperature bias is shown in Figure 3c. Independently of the temperature bias, the heat current increases with the number of sites, but it saturates for $N > 8$. The current values in the steady state are in agreement to those calculated by using the standard Landauer approach (see dashed lines in Figure 3c).

**Polyacetylene (PA) and Polyethylene (PE) Dimers.** In the next step, we demonstrate that our approach can be efficiently combined with first-principles methods to address phonon dynamics in realistic nanoscale systems. As paradigmatic examples, we focus on polyacetylene (PA, four atoms) and polyethylene (PE, six atoms) dimers connected to two harmonic baths, as shown in Figure 4a,b. The main difference between them is the presence of double carbon bonds in the PA junction, whereas the PE junction only contains single carbon bonds. Structural optimizations were
investigated. Our computational scheme allows it to study a variety of topical questions related to nanophononics, such as heat pumping, on an atomistic basis.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b06598.

Derivation of the equations of motion and benchmarking of the spectral density parameters (PDF)

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Notes

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