Quantum Thermal Transport from Classical Molecular Dynamics

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Using a generalized Langevin equation of motion, quantum thermal transport is obtained from classical molecular dynamics. This is possible because the heat baths are represented by random noises obeying quantum Bose-Einstein statistics. The numerical method gives asymptotically exact results in both the low-temperature ballistic transport regime and the high-temperature strongly nonlinear classical regime. The method is a quasiclassical approximation to the quantum transport problem. A one-dimensional quartic on-site model is used to demonstrate the crossover from ballistic to diffusive thermal transport.

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Many approaches have been used to study lattice heat transport in bulk materials and nanostructures. For bulk materials, the standard method is that of Peierls based on Boltzmann equation for phonons [1,2]. For quasi-one-dimensional systems and nanojunctions, a variety of techniques has been used, such as molecular dynamics (MD) [3,4], mode-coupling theory [5], nonequilibrium Green's function (NEGF) method [6–10], Schrödinger equation method [11], quantum Langevin dynamics [12,13], rigorous Boltzmann equations [14], etc. One of the outstanding problems in heat transport is to reconcile the ballistic nature at low temperatures with the diffusive one at high temperatures. As far as we know, the methods mentioned above work only in either the ballistic regime or the diffuse regime, but not in both.

Molecular dynamics has the potential to be such a universal method for heat transport. However, since MD is based on classical Newtonian mechanics, the quantum effect is completely absent. Thus, we cannot expect that it is still correct at low temperatures. In fact, due to a very high Debye temperature for carbon based materials, even 300 K is considered a low temperature. The kinetic theory of heat transport for phonons gives the thermal conductivity as $\kappa = \frac{1}{3} c v l$, where c is heat capacity, v is sound velocity, and l is the mean free path. The reduction of the thermal conductivity at low temperatures is mainly due to the much reduced quantum heat capacity c, but a classical MD can only produce a constant heat capacity.

Can we simulate a quantum system within MD? At first sight, this seems impossible, since classical dynamics can only produce classical results. In this Letter, we show that the heat transport problem in junction systems can be studied with a classical generalized Langevin dynamics using a quantum heat bath derived from Bose-Einstein statistics. Such a treatment is known as a quasiclassical approximation to the quantum Langevin equations [15,16]. Instead of the generic Nosé-Hoover heat bath, it is essential to use the generalized Langevin dynamics with a memory kernel and colored noises to correctly account for the effect of the baths. The heat baths are modeled as infinite numbers of coupled harmonic oscillators. A remarkable feature of the proposed dynamics is that it reproduces the quantum ballistic result at low temperature when nonlinearity can be neglected, as well as gives a correct high-temperature, strongly nonlinear result. This appears to be the only method that is numerically exact in both limits. Our method is inspired by the NEGF approach [9] to heat transport and also the quantum Langevin approach [13] to the same problem.

In the rest of the Letter, we introduce the model and derive the equations involved. We then compare the MD results with Landauer formula and with the nonlinear NEGF results. We treat a one-dimensional (1D) quartic nonlinear on-site model, in which we have seen ballistic transport at temperatures below 200 K, and diffusive transport about 1000 K for lattice sizes up to 4096.

The general setup of our system consists of a central junction region connected to two semi-infinite harmonic lattices which serve as leads. The Hamiltonian of the system is

$$\mathcal{H} = \sum_{\alpha=L,C,R} H_\alpha + (u^L)^T V^{LC} u^C + (u^C)^T V^{CR} u^R + V_n, \tag{1}$$

where $H_\alpha = \frac{1}{2}(\dot{u}^\alpha)^T \dot{u}^\alpha + \frac{1}{2}(u^\alpha)^T K^\alpha u^\alpha$, u^α is a column vector consisting of all the displacement variables in region α ($=L$, C, R), and $\dot{u}^\alpha$ is the corresponding conjugate momentum. The superscript T stands for matrix transpose. We have chosen a renormalized displacement $u_j = \sqrt{m_j} x_j$ where m_j is the mass associated with jth degree of freedom, x_j is the actual displacement having the dimension of length. K^α is the spring constant matrix, and $V^{LC} = (V^{CL})^T$ is the coupling matrix of the left lead to the central region, similarly for V^{CR}. V_n is a nonlinear potential which depends only on u^C. The equations of motion are

$$\ddot{u}^C = -K^C u^C + F_n(u^C) - V^{CL} u^L - V^{CR} u^R, \tag{2}$$

$$\ddot{u}^L = -K^L u^L - V^{LC} u^C, \tag{3}$$

$$\ddot{u}^R = -K^R u^R - V^{RC} u^C. \tag{4}$$

The heat-bath degrees of freedom u^L and u^R can be eliminated by solving them in terms of the central variables and initial conditions, given, e.g., for the left lead

$$u^L(t) = \int_{t_0}^{t} g(t,t') V^{LC} u^C(t') dt' + \frac{\partial g(t,t_0)}{\partial t_0} u^L(t_0) - g(t,t_0)\dot{u}^L(t_0), \tag{5}$$

where the matrix $g(t,t')$ is the time-domain retarded surface Green's function of the left lead obtained by the solution of

$$\frac{\partial^2 g(t,t')}{\partial t'^2} + g(t,t')K^L = -\delta(t-t')I, \tag{6}$$

with the condition $g(t,t') = 0$ if $t - t' \le 0$.

Substituting the formal solutions of the leads into the central region, we obtain the following generalized Langevin equation [13,17,18] for the central part of the degrees of freedom

$$\ddot{u}^C = -K^C u^C + F_n(u^C) - \int_{t_0}^{t} \Sigma(t,t') u^C(t') dt' + \xi_L + \xi_R, \tag{7}$$

where F_n is the nonlinear force, the matrix Σ is the retarded self-energy of the leads, $\Sigma = \Sigma_L + \Sigma_R$, as used in NEGF calculation, but in the time domain; $\Sigma_L = V^{CL} g V^{LC}$. A similar expression holds for the right lead Σ_R using the right lead surface Green's function. Contribution from the left lead due to the initial conditions is

$$\xi_L(t) = V^{CL}\left(g(t,t_0)\dot{u}^L(t_0) - \frac{\partial g(t,t_0)}{\partial t_0} u^L(t_0) \right). \tag{8}$$

The right lead ξ_R is analogous. The initial time t_0 will be set to $-\infty$. Using the concept of adiabatic switch-on, at time $-\infty$, the three subsystems, left lead, central region, and right lead, are decoupled, and the leads are in respective thermal equilibrium. We turn Eq. (7) into a stochastic differential equation by requiring that $u^L(t_0)$ and $\dot{u}^L(t_0)$ are random variables.

So far we have treated the system as a classical system. However, at this point, we will make a departure and consider the leads quantum mechanically. At time $t_0 \to -\infty$, the leads are isolated. We assume that the leads obey a quantum Bose-Einstein statistics. This induces a random vector $\xi_L(t)$ having zero mean, $\langle \xi_L(t) \rangle = 0$, and the following correlation matrix

$$\begin{aligned}\langle \xi_L(t)\xi_L(t')^T \rangle = V^{CL}[&\dot{g}(t,t_0)\langle u^L(t_0)u^L(t_0)^T\rangle \dot{g}(t',t_0)^T \\ &- \dot{g}(t,t_0)\langle u^L(t_0)\dot{u}^L(t_0)^T\rangle g(t',t_0)^T \\ &- g(t,t_0)\langle \dot{u}^L(t_0)u^L(t_0)^T\rangle \dot{g}(t',t_0)^T \\ &+ g(t,t_0)\langle \dot{u}^L(t_0)\dot{u}(t_0)^T\rangle g(t',t_0)^T] V^{LC}.\end{aligned} \tag{9}$$

For a sensible heat bath, the correlation should be time translationally invariant and independent of t_0. Indeed, great simplification can be done if we use the eigenmode representation for the matrix g:

$$g(t,t') = S^T g^d S, \quad g^d_j = -\theta(t-t')\frac{\sin\omega_j(t-t')}{\omega_j}, \tag{10}$$

where S is the orthogonal matrix that diagonalizes K^L, $SK^LS^T = \Omega^2$, Ω^2 is a diagonal matrix with diagonal elements ω_j^2; ω_js are the positive eigenfrequencies. Substituting this result into the correlation expression, also using the quantum equilibrium correlation values for $\langle uu^T\rangle$, $\langle \dot{u}u^T\rangle$, $\langle u\dot{u}^T\rangle$, and $\langle \dot{u}\dot{u}^T\rangle$, we get

$$\langle \xi_L(t)\xi_L(t')^T \rangle = V^{CL} S^T D S V^{LC}, \tag{11}$$

where D is a diagonal matrix with elements $D_j = [f(\omega_j) + \frac{1}{2}]\frac{\hbar}{\omega_j}\cos\omega_j(t-t') + \frac{\hbar}{2i\omega_j}\sin\omega_j(t-t')$. $f(\omega) = [\exp(\hbar\omega/k_BT_L) - 1]^{-1}$ is the Bose-Einstein (or Planck) distribution function at the temperature of the left lead.

We notice that D is complex. The imaginary part comes from the fact that in quantum mechanics, $\xi(t)$ and $\xi(t')$ are noncommuting, and the product of the two is not a Hermitian operator. If we use a symmetrized correlation $\frac{1}{2}\langle \xi_j(t)\xi_l(t') + \xi_l(t')\xi_j(t)\rangle$, it then can be interpreted properly in a classical dynamics. The second term is obtained by interchanging t and t' and taking the transpose. The final effect is simply to drop the imaginary term. The symmetrized correlation together with the classical Langevin equation, Eq. (7), consists of the so-called quasiclassical approximation [15].

Then the question arises that such a treatment will not give correctly the quantum results. For nonlinear systems it is an approximation, but it is exact, at least for the expression of heat current, for linear systems. It can be shown rigorously that, with the symmetrized heat baths, we reproduce the Landauer result with Caroli formula as the transmission coefficient. However, the symmetrization does have a consequence to the quantum heat-current fluctuations.

Using the (surface) density of states, the expression can be further simplified to get a rather compact result for the spectrum of the noises [13],

$$\tilde{F}[\omega] = \int_{-\infty}^{\infty} \langle \xi_L(t)\xi_L^T(0)\rangle e^{i\omega t} dt = \left(f(\omega) + \frac{1}{2}\right)\hbar\Gamma_L[\omega], \tag{12}$$

where $\Gamma_L[\omega] = i(\Sigma_L[\omega] - \Sigma_L[\omega]^\dagger) = -2\mathrm{Im}V^{CL}g[\omega]V^{LC}$.

The spectrum function $\tilde{F}[\omega]$ is even in ω and is a symmetric, positive semidefinite matrix. The classical limit is obtained if we take $[f(\omega) + 1/2]\hbar \approx k_B T_L/\omega$, where k_B is the Boltzmann constant and T_L is the temperature of the left lead.

The thermal current in steady state can be computed in several equivalent ways

$$I_L = -I_R = -\left\langle \frac{dH_L}{dt} \right\rangle = \langle (\dot{u}^L)^T V^{LC} u^C \rangle$$
$$= -\langle u^C(t)^T \dot{b}(t) \rangle = \langle \dot{u}^C(t)^T b(t) \rangle, \tag{13}$$

where $b(t) = -\int_{t_0}^{t} \Sigma_L(t, t') u^C(t') dt' + \xi_L(t)$.

The stochastic differential equation, Eq. (7), can be solved numerically in a straightforward way. Both the memory function (retarded self-energy Σ) and the noise spectrum $\tilde{F}$ can be obtained through the surface Green's function g. Efficient recursive algorithms exist for the solution of g [9,19]. A set of past coordinates, $u^C(t)$, needs to be stored, in order to perform a numerical integration with the self-energy. We can use a simple rectangular rule for the integration. The random noises can be generated using a spectrum method [20]. Let the discrete Fourier transform of $\xi(t)$ be $\eta_k = \eta^*_{-k} = a_k + ib_k$, $k = -M/2, \cdots, -1, 0, 1, \cdots, M/2 - 1$, where M is the number of sampling points in the discrete Fourier transform. Then the noises can be generated by taking real vectors a_k and b_k $(k > 0)$ as independent Gaussian random numbers with zero mean and covariance matrix $\frac{1}{2}\tilde{F}[\omega_k]hM$, where h is the integration step size, and $\omega_k = 2\pi k/(hM)$. The noise values at the required times are obtained by an inverse fast Fourier transform as $\xi(t = hl) = \frac{1}{hM}\sum_k \eta_k \exp(-i2\pi lk/M)$. The numerical integration of Eq. (7) is not substantially more expensive than standard MD. This is because the forces are usually short-ranged; we only need to do the extra work for these sites that are directly connected to the leads.

To illustrate the general method, we consider a 1D model with a quartic on-site potential (ϕ^4 model). Such a model is known to have diffusive transport in the classical limit [21]. The equation of motion is given by

$$\ddot{u}_j = Ku_{j-1} - (2K + K_0)u_j + Ku_{j+1} - \mu_j u_j^3. \tag{14}$$

We divide the system into three regions, $j \le 0, 0 < j \le N$, and $j > N$, as the left lead, central region, and right lead. The nonlinear term is zero in the leads, i.e., $\mu_j = \mu$ if $1 \le j \le N$ and $\mu_j = 0$ otherwise. The relevant spring constant matrices can be read off from Eq. (14), e.g., K^L is tridiagonal with diagonal elements equal to $2K + K_0$ and off-diagonals equal to $-K$; $V^{LC}_{jl} = 0$ except for $V^{LC}_{0,1} = -K$. The required surface Green's function can be obtained analytically in frequency domain as $g_{00}[\omega] = -\lambda/K$, where λ is the root of the quadratic equation, $K\lambda^{-1} + (\omega + i0^+)^2 - 2K - K_0 + K\lambda = 0$, such that $|\lambda| < 1$. The nonzero (1,1) and (N, N) elements for Σ and Γ are obtained from g. We use the following expression for the heat current [3],

$$I^{\mathrm{MD}} = \frac{K}{2}\langle (\dot{u}_j + \dot{u}_{j+1})(u_j - u_{j+1}) \rangle. \tag{15}$$

Because of energy conservation along the chain, one can show that Eq. (15) agrees with the definition, Eq. (13).

We now present our numerical results. First, when the system is linear, $\mu_j \equiv 0$, the heat current can be computed exactly through the Landauer-Caroli formula, $I_L = \frac{1}{2\pi} \times \int_0^\infty d\omega \hbar\omega \mathrm{Tr}(G^r \Gamma_L G^a \Gamma_R)(f_L - f_R)$, where $G^r = (G^a)^\dagger = [(\omega + i0^+)^2 - K^C - \Sigma]^{-1}$. The molecular dynamics with the quantum heat bath reproduces this result exactly. In Fig. 1, we present the comparison of the MD and the exact curve. The conductance is defined by

$$\sigma = \lim_{T_L \to T_R} \frac{I_L}{T_L - T_R}. \tag{16}$$

A numerical finite difference with 10% deviation from the average temperature is used. Within statistical errors (estimated from the fluctuation of multiple runs), the agreement is perfect. For the ballistic transport, the thermal conductance is independent of the lengths N of the chain.

A nontrivial result is obtained when the system has nonlinear interactions. This is presented in Fig. 2. With a nonlinear strength of $\mu = 1$ [eV/(amu^2 Å^4)], we get quantitatively correct result of ballistic transport at low temperatures and small sizes ($\sigma \propto N^0$) and diffusive transport at high temperatures and large sizes ($\sigma \propto 1/N$). The low-temperature results can be compared with the NEGF ones. This is presented as smooth curves in Fig. 2. The NEGF results are computed with a mean-field approximation to the self-energies [9]. The Green's functions are iterated in equilibrium and the conductance is calculated with an approximate formula for the transmission, $\tilde{T}[\omega] = \frac{1}{2}\mathrm{Tr}\{G^r(\Gamma_L + \frac{1}{2}\Gamma_n)G^a\Gamma_R\} + \frac{1}{2}\mathrm{Tr}\{G^a\Gamma_L G^r(\Gamma_R + \frac{1}{2}\Gamma_n)\}$,

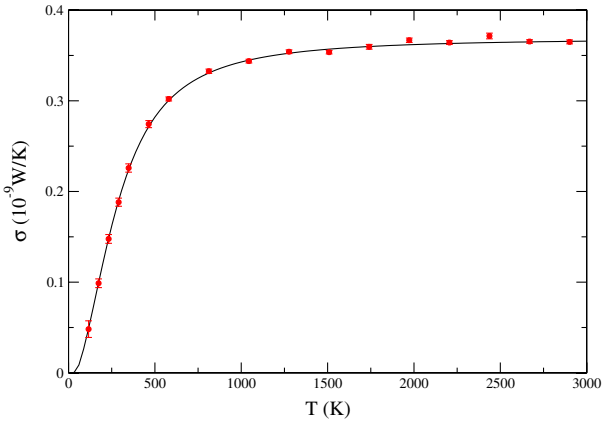

FIG. 1 (color online). Thermal conductance σ as a function of temperature for the 1D on-site model without the nonlinear interaction, with spring constant $K = 1.0$ eV/(amu Å^2), $K_0 = 0.1$ K. The smooth curve is the Landauer formula result, while the symbols are MD results with a size $N = 8$. The time step $h = 10^{-16}$ s and 5×10^8 MD steps each are used.

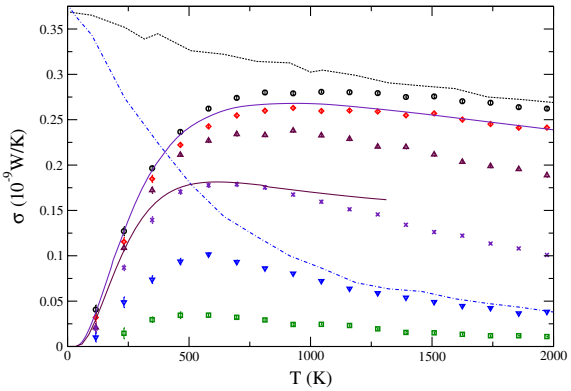

FIG. 2 (color online). Thermal conductance σ for the 1D on-site model with a nonlinear interaction $\mu = 1$ eV/(amu^2 Å^4), spring constant $K = 1.0$ eV/(amu Å^2), $K_0 = 0.1$ K. The smooth curves are the NEGF results for sizes $N = 4$ and 32, respectively, while the symbols are MD results with size N from 4, 16, 64, 256, 1024, to 4096, from top to bottom. The dashed lines are MD results with classical heat bath for size $N = 4$ (top) and 1024 (bottom). The time step $h = 10^{-16}$ s and 10^8 MD steps each are used.

where the nonlinear effect is reflected in the extra nonlinear self-energy, $\Gamma_n = i(\Sigma_n^r - \Sigma_n^a)$. The MD and NEGF results agree with each other at the low-temperature side very well. Clearly, the nonlinear NEGF results are not exact at high temperatures. Thus the deviation there between MD and NEGF is understandable. When classical heat baths are used, then as the temperature decreases, the thermal conductance increases monotonically to a size-independent ballistic limit of $(\omega_{\max} - \omega_{\min})k_B/(2\pi)$, where $\omega_{\max} - \omega_{\min}$ is the phonon band width. The classical and quantum heat-bath results converge to the same value at sufficiently high temperatures. At the intermediate range of temperatures, no reliable methods exist that can be compared with the quantum MD results. In this difficult temperature range, the MD results are the only numbers to offer. Whether we see ballistic or diffusive transport in a given temperature is determined by the mean free path of the phonons in comparison with the system size N. From the data in Fig. 2, we can judge that the mean free path is about 10^3 lattice spacings in the temperature range of 1000 K.

The dynamics (with equal temperatures for the two leads) also gives correctly the quantum average energy using the classical total energy expression as an estimator. By numerical differentiation, we also obtained the correct quantum heat capacity. This is consistent with the fact that quantum conductance is calculated correctly. Data will be presented elsewhere.

In summary, we have shown that a generalized Langevin dynamics from a classical stochastic differential equation can reproduce quantum ballistic transport if the heat baths follow the quantum prescription. This is achievable because there is very little difference between a quantum and a classical system if the system is linear. The dynamics is such that it smoothly crosses over to the classical regime. Thus the method produces correctly results both in the quantum ballistic limit and classical diffusive limit. We have applied the method to a simple 1D on-site model. Clearly, it is generally applicable. For example, we can use the approach to study ballistic and diffusive thermal transport in carbon nanotubes and graphene ribbons. We can also study the nonlinear effect in interfaces. The present method opens new way for studying quantum transport and nonlinearity.

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