Simulation of Nonharmonic Interactions in a Crystal by Self-Consistent Reservoirs*

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Independent heat reservoirs are postulated to interact with the atoms in a harmonic system as a substitute for real nonharmonic forces. The temperature of each reservoir is determined by the condition that it exchange no energy with the system in the steady state. An explicit solution for the covariance matrix is obtained for the case of the linear chain. The thermal conductivity is finite and inversely proportional to the coupling to the reservoirs.

A serious deficiency of the harmonic lattice as a model for real solids is that it is not an ergodic system. The state of the lattice can be expressed as a superposition of normal modes (phonons), and the coefficients of the different normal modes (occupation numbers and phases of phonons) do not change with time. Any harmonic lattice that is started at $t = 0$ away from equilibrium will never approach the canonical equilibrium distribution $e^{-\beta H}$. On the other hand, in the real crystal, phonons can be created and destroyed by anharmonic interactions with other phonons and with the electrons in the solid. Explicit inclusion of these interactions generally makes lattice dynamics problems intractable.

The nonharmonic interactions are the sole mechanism by which an isolated system can approach equilibrium. They facilitate the diffusion in phase space and the dissipation which together bring a system toward equilibrium and keep it there. We propose to simulate these nonharmonic interactions by postulating that each atom in the harmonic crystal interacts stochastically with its own thermal reservoir.

In the classical or high-temperature case, where the interactions of the lattice with the electrons in the crystal are incoherent, the description of the electron-phonon interaction in this way is undoubtedly accurate. Less intuitive is the validity of the replacement of the anharmonic phonon-phonon interactions by stochastic reservoirs at the atoms; it would be more realistic to allow correlations between different reservoirs, but also much more complicated.

A convenient characterization of the reservoirs is by a nonconservative Fokker-Planck force[1] acting on each atom in the crystal. The Fokker-Planck force is equivalent to an impulsive interaction of the atom with a Maxwellian gas of hard particles that are much lighter than the atoms of the crystal, and which collide with the crystal atom frequently compared to the characteristic time of the lattice. The Fokker-Planck force can be written

$$F_i = -M\lambda_i \left(v_i + \frac{1}{M\beta_i} \frac{\partial}{\partial v_i} \right), \qquad (1)$$

where λ_i is the dissipative viscosity parameter,[2] $\beta_i = 1/T_i$ with T_i equal to k times the temperature of the ith reservoir, and Mv_i is the momentum of the ith lattice atom. When it operates on a velocity distribution function, F_i is the sum of an attraction toward the origin in velocity space and a diffusive term that tends to flatten the velocity distribution.

The constants λ_i can, in principle, be related to anharmonic and electron-phonon interactions; to do so would be a complicated task, so we shall simply assume that all the λ_i are equal to a common value that is to be regarded as an adjustable parameter. In some cases, it is useful to allow the λ_i to have a different value at the surface of the system. The value of T_i, on the other hand, determines the energy flow between the lattice and the reservoir at point i. If the reservoir temperature is equal to the local kinetic temperature of the lattice there will be no energy exchange. This is, in fact, the physical situation in the steady state, and we therefore postulate as a condition of our model that T_i be equal to the kinetic temperature at the lattice point i.

The reservoirs supply no heat, entropy, or other thermodynamic quantity to the system. They may be viewed as a device for making the system ergodic. Of course, the ergodicity or nonergodicity of the system does not affect equilibrium properties; on the other hand, it is critical for nonequilibrium phenomena, as will be evident from the following.

As an illustration of the effects of self-consistent reservoirs, we will consider the linear harmonic chain and calculate its simplest nonequilibrium parameter, the thermal conductivity. Our notation is taken from Ref. 3, where it is shown that the

equation determining the evolution of the covariance matrix b is

$$\dot{b}(t) = d - ab(t) - b(t)\tilde{a} \ . \tag{2}$$

Here, $b_{ij}(t)$ is the expectation value at time t of $x_i x_j$, with x the $2N$-dimensional vector of coordinates and momenta with transpose

$$\tilde{x} = (q_1, \ldots, q_N, p_1, \ldots, p_N) \ . \tag{3}$$

In (2), a and d have the forms

$$a = \begin{pmatrix} 0 & -I \\ \Phi & \Lambda \end{pmatrix}, \qquad d = \begin{pmatrix} 0 & 0 \\ 0 & 2\Lambda T \end{pmatrix} \ , \tag{4}$$

where I is the $N \times N$ identity, Λ is the diagonal matrix of the λ_i of Eq. (1), T is the diagonal matrix of the reservoir temperatures, and Φ is the matrix of the harmonic force constants

$$\Phi_{ij} = (2 + \kappa') \delta_{i,j} - \delta_{i,j+1} - \delta_{i,j-1} \ . \tag{5}$$

We have taken both the mass and the interatomic force constant equal to unity; κ' is the force constant binding each atom to its equilibrium position (see Fig. 1).

Equation (2) is solved by setting

$$b = \begin{pmatrix} X & Z \\ \tilde{Z} & Y \end{pmatrix} , \qquad X = \tilde{X}, \qquad Y = \tilde{Y} \ . \tag{6}$$

Then in the steady state with $\dot{b} = 0$, the matrices X, Y, and Z must satisfy the equations

$$2\Lambda T = \Lambda Y + Y\Lambda + \Phi Z - Z\Phi, \tag{7a}$$

$$\Lambda Z + Z\Lambda = \Phi X - X\Phi \ , \tag{7b}$$

$$2Y = X\Phi + \Phi X + Z\Lambda - \Lambda Z \ , \tag{7c}$$
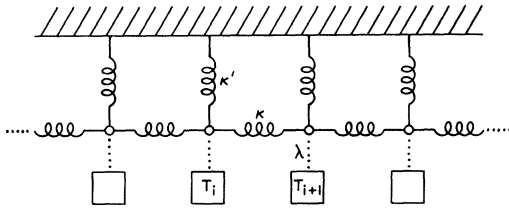
$$\tilde{Z} = -Z \ . \tag{7d}$$

FIG. 1. Model for the harmonic chain with reservoirs. The dotted lines symbolize the action of a Fokker-Planck force.

At least three features of Eqs. (7) are worth emphasizing. First, if the coupling Λ to the reservoirs is turned off, then Z, which contains the heat currents, becomes independent of X and Y, which determine the temperatures of the lattice points. A similar decoupling is evident in Ref. 3, where the coupling Λ is nonzero only at the ends of the chain; then the relation between (X, Y) and Z is determined by the boundary interactions and not at all by internal interactions. Thus, without coupling to internal reservoirs the local heat current is not determined by the local temperature gradient, but rather by conditions at the boundaries of the system. The same conclusion holds for a disordered harmonic system.

Second, Eq. (7c) gives a prescription for determining the potential energy of a lattice particle in such a way that equipartition holds. Since Λ is diagonal, a diagonal element of (7c) gives

$$\tfrac{1}{2} Y_{ii} = \tfrac{1}{4} (X\Phi + \Phi X)_{ii}$$

$$= \tfrac{1}{2} \langle (2 + \kappa') q_i^2 - q_i q_{i+1} - q_i q_{i-1} \rangle \ . \tag{8}$$

The left-hand side is the kinetic energy of the lattice point i, and it follows that if its potential energy is defined by the right-hand side of (8), then local equipartition of energy between kinetic and potential terms holds in this nonequilibrium situation.

Third, the diagonal elements of (7a) give

$$\lambda_i (T_{ii} - Y_{ii}) = Z_{i,i+1} - Z_{i-1,i} \ , \tag{9}$$

and since $Z_{i,i+1}$ is the energy flow between particles i and $i+1$, we see that the energy flow into the reservoir at point i is proportional to the difference between the temperature of the reservoir at i and the kinetic temperature Y_{ii} of the lattice point i.

At this point, rather than imposing self-consistency as a condition on the solution, we will solve Eqs. (7) for a particular imposed external temperature distribution T and show that the resulting kinetic temperatures are equal to the imposed reservoir temperatures in the limit of an infinite chain. More general applications of self-consistent reservoirs will be discussed in future work.

Equations (7) are most easily solved by going to the representation in which Φ is diagonal. For the N-atom chain with fixed ends, Φ is diagonalized by the symmetric orthogonal matrix S

$$S\Phi S = g \ ,$$

$$S_{i\alpha} = \left(\frac{2}{N+1}\right)^{1/2} \sin\frac{\pi i \alpha}{N+1} \ ,$$

$$i = 1, \ldots, N , \quad \alpha = 1, \ldots, N , \qquad (10)$$

$$g_{\alpha\beta} = \left(2 + \kappa' - 2\cos\frac{\pi\alpha}{N+1}\right)\delta_{\alpha,\beta} .$$

In the representation defined by $\bar{X} = SXS$, etc., the solution of Eqs. (7) for the case that $\Lambda = \lambda I$ is given by

$$\bar{X}_{\alpha\beta} = 4\lambda^2 \bar{T}_{\alpha\beta}/D_{\alpha\beta} ,$$

$$\bar{Y}_{\alpha\beta} = 2\lambda^2 \bar{T}_{\alpha\beta}(g_\alpha + g_\beta)/D_{\alpha\beta} , \qquad (11)$$

$$\bar{Z}_{\alpha\beta} = 2\lambda(g_\alpha - g_\beta)\bar{T}_{\alpha\beta}/D_{\alpha\beta} ,$$

with

$$D_{\alpha\beta} = (g_\alpha - g_\beta)^2 + 2\lambda^2(g_\alpha + g_\beta) . \qquad (12)$$

Since the response given by (11) is linear in the reservoir temperatures, it is sufficient to compute the responses to the individual Fourier components. With the imposed temperature distribution

$$T_{ij} = \delta_{i,j} \bar{T} \cos\frac{\pi i\gamma}{N+1} , \qquad (13)$$

it is straightforward to obtain

$$Y_{ij} = \theta_{ij}\delta_{ij} , \qquad (14a)$$

$$X_{ij} = \theta_{ij}/\{2(A^2-1)^{1/2}[A + (A^2-1)^{1/2}]^{|i-j|}\} , \qquad (14b)$$

$$Z_{ij} = \text{sign}(i-j)\cdot\Delta\theta_{ij}/\{2\lambda[A + (A^2-1)^{1/2}]^{|i-j|}\} , \qquad (14c)$$

where $\quad A = 1 + \frac{1}{2}\kappa'$,

$$\theta_{ij} = \bar{T}\cos\frac{\pi\gamma(i+j)}{2(N+1)} , \qquad (15)$$

$$\Delta\theta_{ij} = -\frac{\pi\gamma\bar{T}}{N+1}\sin\frac{\pi\gamma(i+j)}{2(N+1)} .$$

Since θ has the same diagonal elements as T, the solution is self-consistent. The solution of Eqs. (14) is valid in the limit $N \gg \gamma$ and for $|i - j| \ll N$, $|N - 2i| \ll N$, that is, in the part of the chain where the gradient of T is constant over many lattice spacings.

The steady-state heat current can be extracted from Eq. (14c). For i near $\frac{1}{2}N$ it is given by

$$j_i = Z_{i,i+1} = -\frac{\Delta\theta}{2\lambda[A + (A^2-1)^{1/2}]} ,$$

where $\Delta\theta$ is the difference in temperature between adjacent lattice points. The thermal conductivity is equal to $\{2\lambda[A + (A^2-1)^{1/2}]\}^{-1}$ and is finite for $\lambda \neq 0$. For $\lambda = 0$, the infinite thermal conductivity is a well-known property of an ordered harmonic system. It is gratifying to see that a simple and physically reasonable modification of the harmonic model can lead to reasonable nonequilibrium properties.

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[1] J. L. Lebowitz, Phys. Rev. <u>114</u>, 1192 (1959).

[2] In terms of the parameters of the Maxwellian reservoir $\lambda = (4n\sigma/M)(2m/\pi\beta)^{1/2}$, where σ is the collision cross section for reservoir particles with the lattice atom, n is the number density of reservoir particles and m is their mass. Lebowitz (Ref. 1) gives an expression for λ smaller by a factor of 2; this is a misprint (private communication from J. L. Lebowitz).

[3] Z. Rieder, J. L. Lebowitz, and E. Lieb, J. Math. Phys. <u>8</u>, 1073 (1967).