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Generalized Langevin equation for solids. I. Rigorous derivation and main properties

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We demonstrate explicitly that the derivation by Adelman and Doll (AD) [J. Chem. Phys. **64**, 2375 (1976)] of the generalized Langevin equation (GLE) to describe dynamics of an extended solid system by considering its finite subsystem is inconsistent because it relies on performing statistical averages over the entire system when establishing properties of the random force. This results in the random force representing a nonstationary process opposite to one of the main assumptions made in AD that the random force corresponds to a stationary stochastic process. This invalidates the derivation of the Brownian (or Langevin) form of the GLE in AD. Here we present a different and more general approach in deriving the GLE. Our method generalizes that of AD in two main aspects: (i) the structure of the finite region can be arbitrary (e.g., anharmonic), and (ii) ways are indicated in which the method can be implemented exactly if the phonon Green's function of the harmonic environment region surrounding the anharmonic region is known, which is, e.g., the case when the environment region represents a part of a periodic solid (the bulk or a surface). We also show that in general after the local perturbation has ceased, the system returns to thermodynamic equilibrium with the distribution function for region 1 being canonical with respect to an effective interaction between atoms, which includes instantaneous response of the surrounding region. Note that our method does not rely on the assumption made in AD that the stochastic force correlation function depends on the times difference only (i.e., the random force corresponds to a stationary random process). In fact, we demonstrate explicitly that generally this is not the case. Still, the correct GLE can be obtained, which satisfies exactly the fluctuation-dissipation theorem.

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I. INTRODUCTION

In many physical problems, e.g., relaxation of excited local phonons in a solid,[1] interaction of fast projectiles with crystal surfaces,[2–4] chemisorption and decomposition of molecules adsorbed on surfaces,[5–9] or in fracture propagation simulations,[10,11] the most interesting from the physical point of view "central region" (region 1) may be much hotter than the surrounding part of the extended system (region 2) serving as a heat bath. Because of the energy transfer between the two regions, periodic boundary conditions within the molecular-dynamics (MD) simulations are strictly speaking not applicable, and one has to consider the whole extended system explicitly in order to describe the corresponding nonequilibrium process.

A practical solution to this formidable problem was suggested by Adelman and Doll[2] (AD) (hereafter; see also Refs. 3, 4, 12, and 13) who proposed to treat region 2 as harmonic. (Note that a formal problem of coupling of a system to a harmonic "bath" was considered in Refs. 14 and 15; see also Ref. 16 and references therein.) In the case of the harmonic region 2, its dynamics can be solved exactly and hence explicit expressions for the displacements of atoms in region 2 as functions of time $u_2(t)=\|u_j(t)\|$ can be obtained analytically. Here u_2 is the vector column containing three-dimensional vectors u_j of displacements of all atoms in region 2; we shall use hereafter indices j, j', etc. to indicate atoms from region 2. Note that in particular, the time dependence of u_2 comes from the positions of atoms in region 1, $r_1(t)=\|r_i(t)\|$ (the indices such as i, i', etc. are to be used for atoms in region 1), which the solution $u_2(t)=u_2[r_1(t);t]$ explicitly depends upon. After substituting the displacements $u_2(t)$ into equations of motion for atoms in region 1, i.e., equations for $r_i(t)$ $(i\in 1)$, effective equations of motion for $r_1(t)$ are obtained with two additional time-dependent forces: (i) a force $R_1(t)=\|R_i(t)\|$, which depends on initial displacements $u_2(0)$ and velocities $\dot{u}_2(0)$ of atoms in region 2, and (ii) a force depending on the history of dynamics of atoms in region 1 at all times preceding the current time t. The latter integral term if taken by parts can be transformed into a friction force with memory and an additional contribution, which modifies the interaction between atoms of region 1. In turn, the force $R_1(t)$ is considered as a stationary Gaussian distributed stochastic process since it is a linear combination of initial displacements and velocities $u_2(0)$ and $\dot{u}_2(0)$. Thus, equations of motion for atoms in region 1 become Langevin equations (with memory); the friction and stochastic forces correspond to the interaction between atoms in the two regions with the latter becoming stochastic due to unknown initial positions and velocities of atoms in region 2. The balance of these forces helps to maintain the temperature in region 1: The friction forces would remove extra energy from the region, while the stochastic forces do a work on atoms in region 1 whereby bringing energy in. Thus, the Langevin dynamics of atoms in a *finite* region allow mimicking the dynamics of the whole *extended* system implicitly.

The derivation of the generalized Langevin equation (GLE) in AD was based on a number of assumptions: (i) region 1 atoms are also harmonic, i.e., the whole system was in fact considered to be harmonic; (ii) statistical properties of the random force $R_1(t)$ were investigated based on statistical averages $\langle\ldots\rangle$ calculated with respect to the canonical distribution at initial time $t=0$, i.e., it was assumed that uncertainty in the random force originates from the unknown initial atomic positions and velocities, which are assumed to be canonical at temperature T; (iii) when performing statistical averages, the *whole system* $1\cup 2$ was considered; and (iv) the random force $R_1(t)$ was treated as a stationary process, i.e., its average does not depend on time [in fact, it is zero, $\langle R_1(t)\rangle = 0$], whereas the correlation function $\langle R_1(t)R_1^\dagger(t')\rangle$ depends only on the time difference $t-t'$. The fact that the average of the random force is equal to zero is consistent with averaging with respect to the whole harmonic system. However, dependence of the correlation function of the random force only on the time difference was only assumed and never proven.

The fact that statistical averaging is performed with respect to the entire system $1\cup 2$ results in a double statistical averaging with respect to region 1. Indeed, when solving the GLE, MD simulations on region 1 are performed, and various properties of the system are then calculated from the trajectories of atoms in region 1. Thus, statistical averaging corresponding to region 1 is assumed to be done implying ergodicity based on the MD simulations. Therefore, averaging with respect to the positions and velocities of atoms in the entire system $1\cup 2$ is inconsistent. Moreover, as we shall show using an explicit calculation, performing statistical averaging with respect to the entire system results in fact in a nonstationary random process, i.e., the correlation function $\langle R_1(t)R_1^\dagger(t')\rangle$ depends in general on both times, not just on the time difference as was originally thought. Because the assumption of a stationary process associated with the random force was done in AD in deriving their Brownian form of GLE, the finding that this process is in fact nonstationary invalidates their derivation.

Therefore, the main purpose of this paper is to rederive the GLE in a more general and, at the same time, consistent way. This is done: (i) by not assuming that region 1 is harmonic, i.e., atoms in region 1 move in arbitrary ways, and (ii) when performing statistical averages we integrate with respect to the part of the entire phase space corresponding to region 2 only. In doing so, it is assumed that very large region 2 can be considered as in thermodynamic equilibrium at some temperature *T*, while finite region 1 is considered out of thermal equilibrium in general. The plan of the paper is the following. In Secs. II A and II B we rederive the GLE for a finite set of atoms (region 1) interacting and exchanging energy with an extended set of atoms comprising the harmonic region 2. We shall introduce the random force, derive its statistical properties, and obtain a general expression for the friction force with memory. We shall show that the friction force kernel is directly related to the correlation function of the random force, i.e., the fluctuation-dissipation theorem. The only assumption, which we shall need for this is that the interaction between the two regions is linear in displacements of atoms in the harmonic region 2. Thermodynamic equilibrium is considered in Sec. III, while in the following Sec. IV we briefly discuss a possibility of exact implementation of the GLE in MD simulations. Finally, conclusions will be made in Sec. V.

In the second paper of this series[17] we shall derive a simplified version of the GLE in which boundary atoms of region 1 are Langevin atoms while all other atoms are governed by usual Newtonian mechanics.

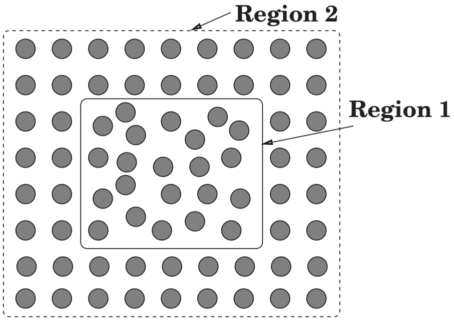

FIG. 1. A finite region 1 where atoms move arbitrarily is surrounded by an extended harmonic region 2 where atoms vibrate about their equilibrium positions.

II. THEORY

A. Derivation of GLE

Consider an extended system of atoms moving around according to the Newtonian dynamics. Most of the system comprising region 2 is assumed to be harmonic, i.e., atoms only vibrate around their equilibrium positions. However, there is also a finite region 1 in which atoms may move arbitrarily, i.e., this may be a "hot spot" where the temperature locally is much higher than in region 2. The schematics of our system are shown in Fig. 1.

The Hamiltonian of the whole system $1\cup 2$ is given by

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 = \mathcal{H}_1 + \frac{1}{2}\sum_{j\in 2} m_j \dot{u}_j^2 + \frac{1}{2}\sum_{j,j'\in 2} u_j \Phi_{jj'} u_{j'} + \sum_{j\in 2} h_j u_j, \tag{1}$$

where the dagger is used to indicate the transposed vectors and matrices, $\mathcal{H}_1 = T_1 + U_1$ is the Hamiltonian of atoms in finite region 1 including their kinetic T_1 and potential U_1 energies. The last three terms in the $\mathcal{H}$ correspond to the Hamiltonian of region 2 $\mathcal{H}_2$. It contains kinetic energy of atoms in the region, their harmonic potential energy (with $\Phi_{jj'}$ being elements of the force-constant matrix Φ_{22} of region 2), and their interaction with atoms in region 1 in the last term. There, $-h_j$ gives the force with which atoms in region 1 act on atom *j*. Of course, the force $-h_j = -h_j[r_1(t)]$ depends on the current positions of all atoms in region 1 given by the vector column $r_1 = \|r_i\|$ and is thus time dependent. Note that we assume that the interaction energy is linear with respect to displacements of atoms in region 2. This is the only approximation (apart from considering region 2 as harmonic, of course), which we make in this section. Note that in Ref. 14 a different case was considered in which the coupling term is linear instead in the atomic coordinates of region 1. As here region 2 is assumed to be harmonic while atoms in region 1 may move under an arbitrary anharmonic potential, we believe the consideration of the coupling to be linear in terms of the atoms in region 2 (the "bath") is more appropriate. Therefore, in the forthcoming treatment we shall use the Hamiltonian given by Eq. (1).

The general idea of deriving the GLE, which we shall pursue here, is similar to that proposed in Refs. 2 and 14: first, equations of motion for atoms in region 2 are solved, then the obtained solutions are substituted into equations of motion for atoms in region 1. Equations of motion for atoms in both regions are obtained in the usual way,

$$m_1 \ddot{r}_1 = f_1 - \sum_{j \in 2} \frac{\partial h_j}{\partial r_1} u_j \tag{2}$$

$$m_2 \ddot{u}_2 = -h_2(t) - \Phi_{22} u_2, \tag{3}$$

where $f_1 = -\frac{\partial U_1}{\partial r_1}$ is the vector column of the force acting on atoms in region 1 due to their interactions with other atoms in the same region, $m_1 = \|m_i\|$ and $m_2 = \|m_j\|$ are diagonal matrices of atomic masses. Note that we use here atomic positions r_1 for atoms in region 1 and displacements vectors u_2 for atoms in region 2. This is because atoms in 1 may move around freely, while atoms in 2 may only oscillate around their equilibrium positions.

By making the substitutions $x_j = \sqrt{m_j} u_j$ and $V_j = h_j / \sqrt{m_j}$ and introducing the dynamical matrix D_{22} with elements $D_{jj'} = \Phi_{jj'} / \sqrt{m_j m_{j'}}$, the equation of motion for atoms in region 2 [Eq. (3)] can be rewritten as

$$\ddot{x}_2 + D_{22} x_2 = -V_2. \tag{4}$$

This equation can be solved for $x_2(t)$ by, e.g., defining eigenvectors e_λ and eigenvalues ω_λ^2, of the dynamical matrix D_{22} introduced on region 2, $D_{22} e_\lambda = \omega_\lambda^2 e_\lambda$, where the eigenvectors satisfy usual relations of orthogonality $e_\lambda^\dagger e_{\lambda'} = \delta_{\lambda\lambda'}$, and completeness $\Sigma_\lambda e_\lambda e_\lambda^\dagger = 1_{22}$, where 1_{22} is the unity matrix defined on region 2. Using normal modes ξ_λ defined via

$$x_2 = \sum_\lambda e_\lambda \xi_\lambda \tag{5}$$

(note that ξ_λ is a scalar with the inverse relation being $\xi_\lambda = e_\lambda^\dagger x_2$), Eq. (4) is diagonalized: $\ddot{\xi}_\lambda + \omega_\lambda^2 \xi_\lambda = -V_\lambda$, where the scalar $V_\lambda = e_\lambda^\dagger V_2$ depends on time via vector V_2. The differential equation for the normal modes is easily solved to yield,

$$\xi_\lambda(t) = A_\lambda e^{i\omega_\lambda t} + B_\lambda e^{-i\omega_\lambda t} - \int_0^t V_\lambda(\tau) \frac{\sin[\omega_\lambda(t-\tau)]}{\omega_\lambda} d\tau,$$

where A_λ and B_λ are constants defined from the initial conditions at $t=0$. Substituting this into Eq. (5) and applying initial conditions, one obtains after some simple algebra,[2,18]

$$x_2(t) = \dot{\Omega}_{22}(t) x_2(0) + \Omega_{22}(t) \dot{x}_2(0) - \int_0^t \Omega_{22}(t-\tau) V_2(\tau) d\tau, \tag{6}$$

where we introduced the matrix

$$\Omega_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda} \sin(\omega_\lambda t), \tag{7}$$

and $x_2(0)$ and $\dot{x}_2(0)$ are initial positions and velocities (mass rescaled) of atoms in region 2. The force on atoms in 1 due to atoms $j \in 2$ on the right-hand side of Eq. (2) is transformed into $-\Sigma_{j\in 2} \frac{\partial h_j^\dagger}{\partial r_1} u_j \equiv -\Sigma_{j \in 2} \frac{\partial V_j^\dagger}{\partial r_1} x_j = -V_{12} x_2$, where $V_{12} = \|V_{ij}\|$ is a rectangular matrix with elements $V_{ij} = \frac{\partial V_j^\dagger}{\partial r_i}$, which in turn constitute 3×3 matrices due to the three Cartesian components of vectors. Note that in general the matrix $V_{12} = V_{12}(t)$ depends on time. Thus, Eq. (2) can easily be transformed by means of Eq. (6) into the following form:

$$m_1 \ddot{r}_1 = f_1 - V_{12}[\dot{\Omega}_{22}(t) x_2(0) + \Omega_{22}(t) \dot{x}_2(0)] + \int_0^t V_{12}(t) \Omega_{22}(t-\tau) V_2(\tau) d\tau. \tag{8}$$

This equation is similar in form to that obtained in AD. To transform this into the Langevin (or Brownian) form, we, following the original derivation of Adelman and Doll, should take the integral by parts. However, we shall do it slightly differently by defining a different matrix,

$$\Lambda_{22}(t) = \int_0^t \Omega_{22}(\tau) d\tau = D_{22}^{-1} - \Pi_{22}(t), \tag{9}$$

where

$$\Pi_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \cos(\omega_\lambda t) \tag{10}$$

is another square matrix defined in region 2. In deriving the second part of Eq. (9), we have made use of the spectral representation for the inverse of the region 2 dynamical matrix: $D_{22}^{-1} = \Sigma_\lambda e_\lambda e_\lambda^\dagger / \omega_\lambda^2$. Since $-\Omega_{22}(t-\tau) d\tau = d\Lambda_{22}(t-\tau)$, integration by parts of the integral in Eq. (8) is easily performed yielding the following another form of the GLE:

$$m_1 \ddot{r}_1 = \tilde{f}_1 + R_1 - \int_0^t V_{12}(t) \Pi_{22}(t-\tau) \dot{V}_2(\tau) d\tau, \tag{11}$$

where

$$\tilde{f}_1 = f_1 + V_{12}(t) D_{22}^{-1} V_2(t) \tag{12}$$

is the effective force acting on atoms in region 1 modified due to their interaction with atoms in region 2 clamped at their instantaneous equilibrium positions. Indeed, equilibrium positions of atoms in region 2 are obtained by setting to zero the derivative of the Hamiltonian (1) with respect to the displacements u_2 of atoms in region 2 yielding $x_2^0 = m_2^{1/2} u_2^0 = -m_2^{1/2} \Phi_{22}^{-1} h_2 = -D_{22}^{-1} V_2$. Therefore, the force given by the second term on the right-hand side of Eq. (2) becomes

$$f_1^{(2_0)}(t) = -V_{12} x_2^0 = V_{12} D_{22}^{-1} V_2(t), \tag{13}$$

which is exactly the second term in the effective force in Eq. (12). Thus, the force f_1 is due to all atoms in region 1 at their actual positions at time t plus the force due to all atoms in the surrounding region 2 clamped at their instantaneous equilibrium positions at the same moment. Note that because of the interaction between atoms in the two regions, equilibrium positions u_2^0 fluctuate with time as atoms in region 1 move around, i.e., the force $f_1^{(2_0)}(t)$ corresponds to the instantaneous response of region 2 to the force from region 1, which changes due to atoms there moving around. Therefore, this part of the force $f_1^{(2_0)}(t)$ is also time dependent.

The second term on the right-hand side of Eq. (11),

$$R_1(t) = -V_{12}(t)[\dot{\Omega}_{22}(t)x_2(0) + \Omega_{22}(t)\dot{x}_2(0) + \Pi_{22}(t)V_2(0)] \tag{14}$$

is the force depending on initial positions and velocities of atoms in region 2 (the first two terms), as well as on the initial positions of atoms in region 1 [the last term: it explicitly depends on the initial forces $-V_2(0)$ defined by atomic positions at $t=0$]. Following the original idea by Adelman and Doll, the force $R_1(t)$ is to be considered as a random process. Its statistical properties will be considered below in Sec. II B. We note here though that in our method the random force acquired an additional (the third) term, which was missing in the original formulation in AD. This term is necessary to ensure that the random force has zero mean (see Sec. II B).

The last term in Eq. (11) has the meaning of a generalized friction force with memory. Indeed, since the time dependence in $V_2(t)$ comes entirely from positions $r_1(t)$ of atoms in region 1, one can write

$$\dot{V}_2(t) = \sum_{i\in 1} \frac{\partial V_2}{\partial r_i}\dot{r}_i \equiv V_{21}(t)\dot{r}_1(t)$$

and, therefore, we obtain

$$m_1\ddot{r}_1 = \tilde{f}_1 + R_1 - \int_0^t \Gamma_{11}(t,\tau)\dot{r}_1(\tau)d\tau, \tag{15}$$

where the friction kernel

$$\Gamma_{11}(t,\tau) = V_{12}(t)\Pi_{22}(t-\tau)V_{21}(\tau) \tag{16}$$

in general depends on both times not just on their difference. Equation (15) is the main result of this section. It generalizes the GLE obtained by Adelman and Doll in that it is not based on any assumptions concerning region 1. Also, as it will become clear in Sec. II B, it has the form consistent with statistical averaging over region 2 rather than over the whole system $1\cup 2$ as in AD. In addition, in order to derive the GLE above, we did not assume that the random process associated with the force R_1 is stationary in time. In fact, as will become clear from Sec. II B, it is not.

B. Statistical properties of the random force

The random force defined by Eq. (14) depends explicitly on initial positions and velocities of atoms in region 2. These are not known. Moreover, for extended systems their number could be very large so that explicit specification of the initial conditions in region 2 becomes impossible. Adelman and Doll[2] suggested a solution to this problem by proposing to treat $R_1(t)$ as a stochastic process instead. The properties of this process can be obtained from the explicit expression for the random force since the stochastic nature of the force originates from the unknown initial positions and velocities of atoms in region 2, which are to be chosen from the corresponding canonical distribution. Although our expression for the random force is different from that used in AD, their basic idea of treating $R_1(t)$ as a stochastic process is still valid. However, before deriving the statistical properties of the random force (and hence of the stochastic process in question), one point has to be clarified first. Indeed, what kind of statistical averaging is to be used?

When calculating classical statistical averages of various functions of coordinates and momenta $A(r,p)$, where the vector columns $r=\binom{r_1}{u_2}$ and $p=m\dot{r}=\binom{m_1\dot{r}_1}{m_2\dot{u}_2}$ correspond to the whole system, one has to integrate over the phase space of the whole system. This can be done by first integrating over the part of the phase space associated with region 2, i.e., over u_2 and $p_2=m_2\dot{u}_2$, and then integration over the variables of region 1 can be performed. In the GLE formulation MD calculations are performed only for atoms in region 1. Therefore, statistical averaging over this part of the phase space is performed in a natural way using trajectories of atoms in region 1 and the well-developed methods of MD (assuming ergodicity). Therefore, what is needed is to perform statistical averaging *only* over region 2 in the GLE equation. This is to be done *prior* to running MD simulations on region 1 because of the interaction term between the two regions in the Hamiltonian [the last term in Eq. (1)]. In other words, when performing the statistical averaging over the region 2 phase space, it is necessary to use the Hamiltonian $\mathcal{H}_2$, which (via the interaction term) depends explicitly on positions of atoms r_1 in region 1. Note that the procedure proposed in AD relies on averaging of the GLE with respect to the entire phase space prior to running MD simulations on region 1, which hence is inconsistent. In addition, it is shown in the Appendix that if this strategy was accepted, then the random force would also not correspond to a stationary process contrary to the assumption made in AD. [This particular assumption was used in AD to derive their Eq. (3.2) needed to transform the GLE from the initial form (2.6) to its final form (4.1a) containing the friction term. We also note a misprint in Eq. (4.1a): the dot is missing above $\mathbf{x}_p(\tau)$ there. See the Appendix for details.]

We assume that region 1 is large and represents a local region out of equilibrium. However, it is still much smaller than region 2. In fact, the latter region is so large that it can be considered in statistical equilibrium and described by a canonical distribution at some temperature T fixed by a thermal bath surrounding the entire system. This means that coordinates and momenta (or velocities) of atoms in region 2 *at initial moment* are distributed according to the following (canonical) probability function (see also Ref. 14):

$$\rho_2(u_2,p_2) = Z_2^{-1}e^{-\beta\mathcal{H}_2}, \tag{17}$$

where $\beta=1/k_BT$ is the inverse temperature and the partition function is

$$Z_2 = \int du_2 \int dp_2 e^{-\beta\mathcal{H}_2(u_2,p_2)} = \int dx_2 \int d\dot{x}_2 e^{-\beta\mathcal{H}_2(x_2,\dot{x}_2)},$$

where in the second passage we have replaced u_2 and p_2 with the coordinates $(x_2,\dot{x}_2)$ introduced in Sec. II A. By virtue of Eq. (5), the positions x_2 are related by a unitary transformation (since the eigenvectors $\{e_\lambda\}$ form an orthonormal set) to the normal coordinates $\{\xi_\lambda\}$. Similarly for their time derivatives $\{\dot{\xi}_\lambda\}$. Therefore, the Jacobian of the transformation from the set $(x_2,\dot{x}_2)$ to $(\xi_\lambda,\dot{\xi}_\lambda)$ is equal to unity, and hence integration in the phase space can be performed with respect to the normal coordinates and their velocities,

$$Z_2 = \prod_\lambda \int d\xi_\lambda \int d\dot{\xi}_\lambda e^{-\beta \mathcal{H}_\lambda(\xi_\lambda,\dot{\xi}_\lambda)} = \prod_\lambda Z_\lambda, \tag{18}$$

where

$$\mathcal{H}_\lambda = \frac{1}{2}\dot{\xi}_\lambda^2 + \frac{1}{2}\omega_\lambda^2 \xi_\lambda^2 + V_\lambda \xi_\lambda \tag{19}$$

is the Hamiltonian corresponding to the given normal coordinate λ. Indeed, since region 2 is harmonic, the Hamiltonian $\mathcal{H}_2 = \Sigma_\lambda \mathcal{H}_\lambda$ is exactly equal to the sum of the Hamiltonians associated with each normal coordinate. One can see then that $\mathcal{H}_\lambda$ corresponds to the "displaced" harmonic oscillator, so that all the necessary statistical averages can be calculated analytically. We obtain

$$\langle \xi_\lambda(0) \rangle = \prod_{\lambda_1} \int d\xi_{\lambda_1} \int d\dot{\xi}_{\lambda_1} \rho_2(\{\xi_{\lambda_1}\},\{\dot{\xi}_{\lambda_1}\}) \xi_\lambda = -\frac{V_\lambda(0)}{\omega_\lambda^2}, \tag{20}$$

$$\langle \dot{\xi}_\lambda(0) \rangle = 0, \quad \langle \xi_\lambda(0) \dot{\xi}_{\lambda'}(0) \rangle = 0, \tag{21}$$

$$\langle \xi_\lambda(0) \xi_{\lambda'}(0) \rangle = \frac{\delta_{\lambda\lambda'}}{\beta\omega_\lambda^2} + \frac{V_\lambda(0)}{\omega_\lambda^2}\frac{V_{\lambda'}(0)}{\omega_{\lambda'}^2}, \tag{22}$$

$$\langle \dot{\xi}_\lambda(0) \dot{\xi}_{\lambda'}(0) \rangle = \frac{\delta_{\lambda\lambda'}}{\beta}. \tag{23}$$

Owing to the unitary transformation [Eq. (5)] relating the normal coordinates and their time derivatives to the coordinates x_2 and velocities $\dot{x}_2$ of atoms in region 2, one can easily calculate the required statistical averages (at $t=0$) for these,

$$\begin{aligned}\langle x_2(0) \rangle &= \sum_\lambda e_\lambda \langle \xi_\lambda(0) \rangle = -\sum_\lambda \frac{e_\lambda V_\lambda(0)}{\omega_\lambda^2} \\ &= -\sum_\lambda \frac{e_\lambda [e_\lambda^\dagger V_2(0)]}{\omega_\lambda^2} = -D_{22}^{-1} V_2(0),\end{aligned} \tag{24}$$

$$\langle \dot{x}_2(0) \rangle = 0, \quad \langle x_2(0) \dot{x}_2^\dagger(0) \rangle = 0, \tag{25}$$

$$\langle \dot{x}_2(0) \dot{x}_2^\dagger(0) \rangle = \frac{1}{\beta} 1_{22}, \tag{26}$$

$$\langle x_2(0) x_2^\dagger(0) \rangle = \frac{1}{\beta} D_{22}^{-1} + [D_{22}^{-1} V_2(0)][D_{22}^{-1} V_2(0)]^\dagger, \tag{27}$$

where 1_{22} is the unity matrix defined in region 2.

The expressions obtained above allow for a detailed analysis to be performed on the random force of Eq. (14). First of all, we see that the random force is a linear combination of the atomic displacements and velocities at the initial time $x_2(0)$ and $\dot{x}_2(0)$. These are in turn expressed linearly via the normal coordinates and their velocities ξ_λ and $\dot{\xi}_\lambda$. The latter are distributed according to the Hamiltonian $\mathcal{H}_\lambda$, i.e., we have a Gaussian distribution with the zero mean for $\dot{\xi}_\lambda$ and another Gaussian with the mean from Eq. (20) for ξ_λ. The last term in the definition of the random force does not depend on the variables related to region 2 and should thus be treated as a constant. Hence, the random force is also a Gaussian distributed stochastic variable, and to characterize it completely, it is sufficient to calculate its first two moments. These can be calculated easily from the definition of the random force [Eq. (14)] and the averages for the displacements and velocities of atoms in region 2 obtained above and summarized in Eqs. (24)–(27). One should also use the identities,

$$D_{22}^{-1} \dot{\Omega}_{22}(t) = \dot{\Omega}_{22}(t) D_{22}^{-1} = \Pi_{22}(t), \tag{28}$$

$$\dot{\Omega}_{22}(t) D_{22}^{-1} \dot{\Omega}_{22}(t') + \Omega_{22}(t) \Omega_{22}(t') = \Pi_{22}(t-t'), \tag{29}$$

which are verified using spectral representations of the matrices involved and the fact that eigenvectors e_λ are orthonormal. Thus, we obtain,

$$\langle R_1(t) \rangle = 0, \tag{30}$$

$$\langle R_1(t) R_1^\dagger(t') \rangle = \frac{1}{\beta} V_{12}(t) \Pi_{22}(t-t') V_{21}(t'). \tag{31}$$

We see that in general the random force is *not* a stationary process in our formulation. It will only become the one if V_{12} does not depend on time. This is the case if region 1 is harmonic (see Sec. III); another case is considered in Ref. 17.

Since $\Pi_{22}(0) = D_{22}^{-1}$ [see Eq. (10)], we have for the dispersion matrix of the force at time t the following expression:

$$S_{11} = \langle R_1(t) R_1^\dagger(t) \rangle = \frac{1}{\beta} V_{12}(t) D_{22}^{-1} V_{21}(t). \tag{32}$$

The distribution function for the random force is thus a multidimensional Gaussian,

$$P(R_1; t) \sim \exp\left(-\frac{1}{2} R_1^\dagger S_{11}^{-1} R_1\right) \tag{33}$$

with the dispersion matrix S_{11} being exactly proportional to the temperature; see Eq. (32).

One can see that although the random force fluctuates around zero, the spread of the force given by the matrix $S_{11}(t)$ actually depends on time via $V_{12}(t)$, i.e., the quantity that characterizes interaction between the two regions. We shall see in Sec. III that V_{12} becomes time independent if region 1 is also assumed to be harmonic, in which case the dispersion becomes constant. We note in passing (see a more comprehensive discussion in Ref. 17) that in this case the force autocorrelation function [Eq. (31)] would depend only on the time difference, i.e., the stochastic process becomes stationary. We reiterate again at this point that this is only the case if statistical averaging is performed over region 2; if it is performed over the entire system as in AD, the stochastic process is never stationary even for a harmonic solid as is shown in the Appendix.

Comparing Eqs. (16) and (31), we notice that the kernel of the friction force in Eq. (15) is in fact exactly proportional to the correlation function of the random force,

$$\Gamma_{11}(t,t') = \beta\langle R_1(t)R_1^{\dagger}(t')\rangle. \tag{34}$$

This observation brings us to the final form of the GLE, which has been derived here without any particular assumptions concerning region 1 and the behavior of the random force,

$$m_1\ddot{r}_1 = \tilde{f}_1 + R_1 - \beta\int_0^t \langle R_1(t)R_1^{\dagger}(\tau)\rangle\dot{r}_1(\tau)d\tau. \tag{35}$$

This is an exact result, which follows rigorously from the Hamiltonian (1). Note that our GLE looks slightly different than that given by Eq. (4.1a) in AD: First, the kernel of the friction force is defined differently (it is given as an integral of $\Omega(\tau)$ from t to ∞ in AD, while we have defined it as an integral from zero to t [Eq. (9)]) and, second, we do not have a term containing initial positions of atoms in region 1. It is easy to show, however, that these two forms of the GLE are exactly equivalent: The extra term disappears if the friction kernel is defined as in Eq. (9).

The obtained GLE is the central result of this paper. Our derivation is more general than that provided previously in AD since it is not based on two specific assumptions made there that: (i) atoms in region 1 are harmonic and (ii) the stochastic process associated with the random force is stationary. We show that these two assumptions can be lifted and still the correct GLE can be obtained. In particular, we explicitly prove that the friction kernel is directly related to the autocorrelation function of the random force, which is a manifestation of the second fluctuation-dissipation theorem.[19] Thus, the GLE obtained in AD should have much wider applicability than it has been previously thought.

III. THERMODYNAMIC EQUILIBRIUM

Our treatment would be incomplete if we do not consider what should happen to our system after the local perturbation has ceased. For instance, one can consider a local "hot" spot in region 1 on a surface created by an ion bombardment (e.g., sputtering). One would expect that over some time *after* this process the system should return to thermodynamic equilibrium with the same temperature as in region 2 surrounding region 1. This is because the local region (region 1) is much smaller than region 2 (the heat bath), so that the energy transferred to region 1 would disperse in the whole system without noticeable increase in the temperature in the entire macroscopic system. We shall show in this section that at long times, atoms in region 1 are described by a canonical distribution with some effective interaction corresponding to instantaneous response of atoms in region 2 to the forces from atoms in region 1. This would generalize the original proof given in AD where region 1 was considered as harmonic during all times.

The important point to stress here is that our heat bath (region 2) is considered as strictly harmonic. This means that we limit ourselves to solid systems at not too high temperatures only. After the extra energy received by atoms in region 1 has propagated into region 2, the region 1 atoms would become oscillating around some equilibrium positions, i.e., region 1 would become harmonic as well. Let t_0 be some critical time indicating the atoms in region 1 become harmonic. At all times atoms in region 1 are described by the GLE (15). It contains the integral friction term, which can be split into two contributions, before and after t_0,

$$\int_0^t \Gamma_{11}(t,\tau)\dot{r}_1(\tau)d\tau = \int_0^{t_0} \Gamma_{11}(t,\tau)\dot{r}_1(\tau)d\tau + \int_{t_0}^t \Gamma_{11}(t,\tau)\dot{r}_1(\tau)d\tau.$$

The kernel $\Gamma_{11}(t,\tau)$ is proportional to the correlation function of the random force [Eq. (34)] and should decay to zero at long times differences $t-\tau$ [because of $\Pi_{22}(t-\tau)$ in $\Gamma_{11}(t;\tau)$; see Eqs. (31) and (34)]. Therefore, for $t > t_0$ we can neglect the contribution to the dynamics from the previous times $0 < \tau < t_0$ in the memory term above (i.e., the first integral). This means that we can consider the integration in the integral friction term in Eq. (15) only over the times when region 1 is considered to be harmonic, i.e., $t_0 < \tau < t$. Introducing the time shift $t-t_0 \to t$, we can rewrite the GLE (15). It will take exactly the same form; however, the meaning of the time t will be different: it will be measured from the instant t_0. Since region 1 is now harmonic, we can replace the vector column of atomic positions r_1 with the vector column of atomic displacements u_1. Also, the force f_1 due to other atoms in region 1 can be written explicitly as $f_1 = -\Phi_{11}u_1$, where Φ_{11} is the corresponding force-constant matrix corresponding to the current set of equilibrium positions of atoms in region 1. Further, the interaction between the two regions $V_2 = \|V_j\|$ can also be explicitly written as

$$V_j = \frac{1}{\sqrt{m_j}}h_j = \frac{1}{\sqrt{m_j}}\sum_{i\in 1}\Phi_{ji}u_i = \sum_{i\in 1}\sqrt{m_i}D_{ji}u_i, \quad j \in 2, \tag{36}$$

so that elements V_{ij} of the matrix $V_{12} = \|V_{ij}\|$ become

$$V_{ij} = \frac{\partial V_j}{\partial u_i} = \frac{1}{\sqrt{m_j}}\Phi_{ij} = \sqrt{m_i}D_{ij}, \quad i \in 1, \ j \in 2, \tag{37}$$

i.e., the matrix $V_{12} = m_1^{1/2}D_{12}$ does not longer depend on time. Consequently, the friction kernel $\Gamma_{11}(t,\tau)$ becomes explicitly depending only on the time difference $t-\tau$ (and as a by-product of considering region 1 as harmonic, the stochastic process associated with the random force becomes strictly stationary as has already been mentioned in Secs. II A and II B). Therefore, Eq. (15) takes the following form:

$$\ddot{x}_1 + \tilde{D}_{11}x_1 = \tilde{R}_1 - \int_0^t \tilde{\Gamma}_{11}(t-\tau)\dot{x}_1(\tau)d\tau, \tag{38}$$

where for convenience we introduced a mass-scaled atomic displacement vector $x_1 = m_1^{1/2}u_1$ (recall that m_1 is a diagonal matrix of atomic masses). Correspondingly, other quantities have been scaled as well: $\tilde{R}_1 = m_1^{-1/2}R_1$, and

$$\tilde{\Gamma}_{11}(t) = D_{12}\Pi_{22}(t)D_{21}. \tag{39}$$

Note that the kernel is an even function of time due to Eq. (10) and is also a symmetric matrix. The effective dynamical matrix

$$\tilde{D}_{11} = D_{11} - D_{12}D_{22}^{-1}D_{21} \tag{40}$$

corresponds to atoms in region 2 occupying instantaneous equilibrium positions following current positions $u_1(t)$ of atoms in region 1, i.e., this accounts for a static instantaneous response of region 2 to the movement of atoms in region 1 (the *dynamics* of region 2 is taken care of by the friction and random forces).

Equation (38) can be solved using the Laplace transform (LT) method as in Refs. 2 and 20 to yield,

$$x_1(t) = \xi_{11}(t)x_1(0) + \chi_{11}(t)\dot{x}_1(0) + \int_0^t \chi_{11}(t-\tau)\tilde{R}_1(\tau)d\tau. \tag{41}$$

Applying $t=0$ to this equation, one immediately gets $\chi_{11}(0)=0$ and $\xi_{11}(0)=1_{11}$, where 1_{11} is the unit matrix defined in region 1. Differentiating $x_1(t)$, we get the velocity

$$\dot{x}_1(t) = \dot{\xi}_{11}(t)x_1(0) + \dot{\chi}_{11}(t)\dot{x}_1(0) + \int_0^t \dot{\chi}_{11}(t-\tau)\tilde{R}_1(\tau)d\tau. \tag{42}$$

Again, using $t=0$ we obtain $\dot{\chi}_{11}(0)=1_{11}$ and $\dot{\xi}_{11}(0)=0$. In the above equations, $\chi_{11}(t)=\mathcal{L}^{-1}[\chi_{11}(s)]$ is defined as the inverse LT of the matrix

$$\chi_{11}(s) = [s^2 1_{11} + \tilde{D}_{11} + s\tilde{\Gamma}_{11}(s)]^{-1}, \tag{43}$$

where $\tilde{\Gamma}_{11}(s)=\mathcal{L}[\tilde{\Gamma}_{11}(t)]$ is the LT of $\tilde{\Gamma}_{11}(t)$. The other time-dependent matrix used in the solutions [Eqs. (41) and (42)] is given by

$$\xi_{11}(t) = \mathcal{L}^{-1}\{\chi_{11}(s)[s1_{11} + \tilde{\Gamma}_{11}(s)]\} = 1_{11} - \left[\int_0^t \chi_{11}(\tau)d\tau\right]\tilde{D}_{11}. \tag{44}$$

In addition, by calculating the statistical averages (taken over region 2 as before), we find that

$$\langle x_1(t)x_1^\dagger(0)\rangle = \xi_{11}(t)\langle x_1(0)x_1^\dagger(0)\rangle,$$

$$\langle x_1(t)\dot{x}_1^\dagger(0)\rangle = \chi_{11}(t)\langle \dot{x}_1(0)\dot{x}_1^\dagger(0)\rangle,$$

i.e., the functions $\chi_{11}(t)$ and $\xi_{11}(t)$ are proportional to the appropriate correlation functions defined in region 1 and hence should decay to zero at long times. Note that this behavior is to be expected for a small enough friction. Indeed, for a function to decay to zero as $t\to\infty$, it is sufficient that all its poles have real part to be negative. If we drop the friction kernel in Eq. (43), the poles of $\chi_{11}(s)$ [obtained as roots of $\det \chi_{11}^{-1}(s)=0$] would be pure imaginary and equal to $\pm i\tilde{\omega}_\lambda$, where $\tilde{\omega}_\lambda^2$ are the eigenvalues of the positively defined matrix $\tilde{D}_{11}$. A small positively defined friction kernel in Eq. (43) shifts all poles to the left on the complex plane. This can easily be shown to be true in one dimension (a harmonic oscillator with friction) or in the case when all eigenvalues of $\tilde{\Gamma}_{11}(s)$ are the same. Unfortunately, no general proof of this statement we have been able to find.

Therefore, the first two terms on the right-hand sides of Eqs. (41) and (42) corresponding to initial conditions can be dropped at long times leading to $x_1(t)$ and $\dot{x}_1(t)$ being given by the integral terms only. Since the random force represents a Gaussian process and, as it follows from Eqs. (41) and (42), the displacements $x_1(t)$ and the velocities $\dot{x}_1(t)$ are proportional to the random force $\tilde{R}_1(t)$, they also represent a Gaussian process with the distribution function

$$\mathcal{P}_1(x_1,\dot{x}_1) \sim \exp\left(-\frac{1}{2}y^\dagger\sigma^{-1}y\right), \tag{45}$$

where $y(t)=\binom{y_a}{y_b}=\binom{x_1(t)}{\dot{x}_1(t)}$ and the dispersion matrix $\sigma(t)=\langle y(t)y^\dagger(t)\rangle=\begin{pmatrix}\sigma_{aa} & \sigma_{ab}\\ \sigma_{ba} & \sigma_{bb}\end{pmatrix}$. Using the method developed in Ref. 20, it is possible to calculate the dispersion matrix. After some rather lengthy algebra, we obtain

$$\begin{aligned}\sigma_{aa}(t) &= \langle x_1(t)x_1^\dagger(t)\rangle\\ &= -\frac{1}{\beta}[\chi_{11}(t)\chi_{11}^\dagger(t) + \xi_{11}(t)\tilde{D}_{11}^{-1}\xi_{11}^\dagger(t)] + \frac{1}{\beta}\tilde{D}_{11}^{-1},\end{aligned} \tag{46}$$

$$\sigma_{ab}(t) = \langle x_1(t)\dot{x}_1^\dagger(t)\rangle = \frac{1}{\beta}[\xi_{11}(t)\chi_{11}^\dagger(t) - \chi_{11}(t)\dot{\chi}_{11}^\dagger(t)] = \sigma_{ba}^\dagger(t), \tag{47}$$

$$\begin{aligned}\sigma_{bb}(t) &= \langle \dot{x}_1(t)\dot{x}_1^\dagger(t)\rangle\\ &= -\frac{1}{\beta}[\chi_{11}(t)\tilde{D}_{11}\chi_{11}^\dagger(t) + \dot{\chi}_{11}(t)\dot{\chi}_{11}^\dagger(t)] + \frac{1}{\beta}1_{11}.\end{aligned} \tag{48}$$

Due to decay of both functions $\chi_{11}(t)$ and $\xi_{11}(t)$ to zero when $t\to\infty$, we find that

$$\sigma^{-1} \to \begin{pmatrix}\frac{1}{\beta}\tilde{D}_{11}^{-1} & 0\\ 0 & \frac{1}{\beta}1_{11}\end{pmatrix}^{-1} = \begin{pmatrix}\beta\tilde{D}_{11} & 0\\ 0 & \beta 1_{11}\end{pmatrix}$$

in this limit, so that the distribution function (45) becomes

$$\mathcal{P}_1(x_1,\dot{x}_1) \sim \exp\left[-\frac{\beta}{2}x_1^\dagger\tilde{D}_{11}x_1 - \frac{\beta}{2}\dot{x}_1^\dagger\dot{x}_1\right] \tag{49}$$

at long enough times. Consequently, the distribution function for the displacements $u_1=m_1^{-1/2}x_1$ and the momenta $p_1=m_1\dot{u}_1=m_1^{1/2}\dot{x}_1$ at long times is found to be *canonical*, i.e.,

$$\mathcal{P}_1(u_1,p_1) = \frac{1}{Z_1}e^{-\beta\tilde{\mathcal{H}}_1}, \quad Z_1 = \int du_1dp_1e^{-\beta\tilde{\mathcal{H}}_1}, \tag{50}$$

with the effective Hamiltonian

$$\widetilde{\mathcal{H}}_1 = \frac{1}{2}u_1^\dagger \widetilde{\Phi}_{11} u_1 + \frac{1}{2} p_1^\dagger m_1^{-1} p_1 \tag{51}$$

for region 1, which takes account of the interactions between atoms in the two regions: the effective force-constant matrix here $\widetilde{\Phi}_{11}=\Phi_{11}-\Phi_{12}\Phi_{22}^{-1}\Phi_{21}$ [cf. Eq. (40)] corresponds to atoms in region 2 responding instantly to the positions of atoms in region 1.

In fact, it is easy to show by a direct calculation[18] that the distribution (50) is also a probability for the atoms in region 1 to have definite displacements u_1 and momenta $p_1=m_1\dot{u}_1$, while the displacements and momenta in region 2 are not specified (arbitrary). Indeed, by integrating the canonical distribution of the entire harmonic system over the displacements u_2 and momenta $p_2=m_2\dot{u}_2$ of its subsystem (region 2), one obtains exactly Eq. (50) with the effective force-constant matrix. This proves that the distribution (50) does indeed correspond to considering the *whole* system $1\cup 2$ as canonical when thermodynamical equilibrium is reached.

Thus, we see that—as expected—after the perturbation has ceased, the system returns to the thermal equilibrium described by the canonical distribution corresponding to the same temperature T as that of the heat bath. In fact, we see that considering region 2 as having a definite temperature T means that it serves as a heat bath for the finite region 1.

IV. IS THE EXACT TREATMENT OF THE THERMAL BATH POSSIBLE?

The question we pose here is this: is it possible to implement the exact GLE (35) without making any simplifications, i.e., with the actual heat bath and the memory (non-Markovian) effects fully included? The main problem is related to the calculation of the friction kernel (16) and performing lattice summations over the atoms in region 2, so that calculations presented so far in the literature are based on various approximations (see, e.g., Ref. 4). A numerical method of calculating the friction kernel from a special set of MD simulations was suggested in Ref. 21. A sketch of ideas presented in this section on a possibility of implementing the GLE exactly generalizes those proposed recently in Ref. 22.

If one could derive all the necessary expressions for $V_{12}(t)$, $\Pi_{22}(t)$, and D_{22}^{-1}, then a typical time step in the MD simulation would proceed as follows:

1. Positions and velocities of atoms in region 1 from the previous time step are known (in fact, we need to know velocities over the entire history of the simulation because of the memory term in the GLE; see below).

2. Calculate the dispersion matrix $S_{11}=\|S_{i\alpha,i'\alpha'}\|$ according to Eq. (32) and then draw at random the force vector $R_1=\|R_{i\alpha}\|$ for each atom $i\in 1$ and each its Cartesian component $\alpha=x,y,z$ from the multidimensional Gaussian distribution (33); as this may be difficult to do in practice, random forces $R_{i\alpha}$ for every component $\alpha=x,y,z$ of each atom $i\in 1$ may be drawn at random separately taking only diagonal elements of the dispersion matrix in which case the different forces become independent and are described by single Gaussians

$$P(R_{i\alpha}) = \frac{1}{\sqrt{2\pi}\sigma_{i\alpha}} \exp\left(-\frac{R_{i\alpha}^2}{2\sigma_{i\alpha}^2}\right),$$

with the dispersion $\sigma_{i\alpha}=\langle R_{i\alpha}^2(t)\rangle=\frac{1}{\beta}[V_{12}(t)\Pi_{22}(0)V_{21}(t)]_{i\alpha,i\alpha}$.

3. Calculate the memory term by discretizing the integral:[18]

$$\int_0^t \Gamma_{11}(t-\tau)v_1(\tau)d\tau$$
$$\simeq \left[\frac{1}{2}\Gamma_{11}(t_N-t_1)v_1(t_1) + \sum_{n=2}^{N-1}\Gamma_{11}(t_N-t_n)v_1(t_n) + \frac{1}{2}\Gamma_{11}(0)v_1(t_N)\right]\Delta t,$$

where the index n counts the time steps and the time t happens at the Nth step; we see that knowledge of all velocities $v_1(t_n)$ at the preceding time steps is necessary.

4. Calculate the force $\widetilde{f}_1$ from Eq. (12).

5. Evolve the positions and velocities of atoms in region 1: store the velocities for later use.

Therefore, the actual question is whether or not one can calculate all the necessary matrices such as D_{22}^{-1} and $\Pi_{22}(t)$, which are related to the eigenvectors and eigenvalues of the dynamical matrix D_{22}, defined on region 2 only. The obvious difficulty is that region 2 is very large and solution of the corresponding eigenproblem is not possible. To show the method, which circumvents this problem, we shall consider the simplest case of region 2 being a part of a periodic solid. For instance, one can consider region 1 being some fragment of a crystalline bulk or a small part of a crystal surface; the rest of the system constituting region 2 contains periodically repeated unit cells. In this case we can, as the *reference system*, consider the perfect system in which atoms in region 1 occupy their lattice sites as well; this will be referred to as region 1_0, i.e., the whole reference system is in fact a perfect bulk or surface $1_0\cup 2$. Note that regions 1 and 1_0 may be quite different not only in atomic positions but also in the numbers of atoms of different species. Then, one can calculate the phonon Green's function of the reference system $G(z)=Q(z)^{-1}=(z1-D)^{-1}$, where the dynamical matrix $D=\begin{pmatrix} D_{1_01_0} & D_{1_02} \\ D_{21_0} & D_{22}\end{pmatrix}$ is defined in both regions 1_0 and 2. The important point is that because the Green's function is defined on the whole periodic system, it can be actually calculated. This can be done by going into the **k**-points representation instead of the site representation needed here. The required inverse transformation to the site representation is performed in the usual way via the Brillouin-zone (BZ) integration.

We shall now show that all the matrices of interest can actually be expressed via the Green's function of the reference system. Indeed, consider first the LT of $\Omega_{22}(t)$ defined by Eq. (7),

$$\mathcal{L}[\Omega_{22}(t)] = \Omega_{22}(s) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{s^2+\omega_\lambda^2} = (s^2 1_{22} + D_{22})^{-1}$$
$$\equiv -[(-s^2)1_{22} - D_{22}]^{-1}.$$

It is clearly seen then that $\Omega_{22}(s)$ is directly related to the inverse of the 22 block of the $Q(z)$ matrix defined above:

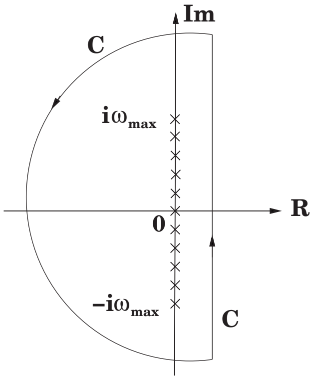

FIG. 2. Integration contour in Eq. (54). The crosses on the imaginary axis represent the poles of the matrix $\Pi_{22}(s)$ of Eq. (53) ($s=0$ and $s=\pm i\omega_\lambda$), which are constrained from above and below by the maximum phonon frequency of the system $\omega_{\max}$.

$\Omega_{22}(s)=-[Q_{22}(z)]^{-1}$ at $z=-s^2$. On the other hand, writing the identity $Q(z)G(z)=1$ by blocks, one can express $Q_{22}^{-1}(z)$ via the blocks of the Green's function yielding the following connection:

$$\Omega_{22}(s) = -G_{22}(-s^2) + G_{21_0}(-s^2)G^{-1}_{1_01_0}(-s^2)G_{1_02}(-s^2). \tag{52}$$

Note that calculation (in the Laplace space) of any element of $\Omega_{22}(s)$ involves only inversion of a finite (in region 1_0) matrix and matrix multiplications with respect to the same finite region. We also note that in particular $D_{22}^{-1}=\Omega_{22}(s=0)$, so that it can be directly calculated from Eq. (52). The LT of $\Pi_{22}(t)$ given via Eq. (10) is related to the LT of $\Omega_{22}(t)$ as follows:

$$\mathcal{L}[\Pi_{22}(t)] = \Pi_{22}(s) = \frac{1}{s}[\Omega_{22}(s=0) - \Omega_{22}(s)]. \tag{53}$$

Hence, using the last two equations, the matrix $\Pi_{22}(s)$ can be expressed via the reference system Green's function and thus can be calculated. The calculation of $\Pi_{22}(t)$ is done using the complex plane contour integration as shown in Fig. 2,

$$\Pi_{22}(t) = \frac{1}{2\pi i}\int_C \Pi_{22}(s)e^{st}ds. \tag{54}$$

The advantage in using this formula is that the integration can be performed numerically as usually functions behave quite smoothly in the complex plane far from their poles. Another method of calculating numerically the inverse LT based on an expansion in Laguerre polynomials[23] was implemented in Ref. 22.

Finally, we note that all summations over region 2 [which appear in matrix multiplications such as, e.g., $V_{12}\Pi_{22}(t)$] can be performed numerically by transforming $\Pi_{22}(t)$ into the **k** representation and then the lattice sums over lattice translations of region 2 can be turned into integrals over the BZ.

Thus, we have shown that in principle one should be able to run dynamics of region 1 with detailed account of its surrounding (region 2). Of course, the implementation of the complete scheme is not straightforward and still work needs to be done to build reasonable approximations. As the first step, the stochastic boundary condition model to be discussed in Ref. 17 could be used.

V. DISCUSSION AND CONCLUSIONS

In this paper we have revisited the derivation of the GLE written for solids originally by AD.[2] They considered a particular situation in which a finite region of a crystal or of its surface (region 1) is substantially perturbed by some external conditions (e.g., ion bombardment), while a very big surrounding part of the system (region 2) is assumed to be harmonic and kept at some temperature T serving as a heat bath for region 1. They made two important assumptions, which allowed them to derive the GLE. First, it was assumed that region 1 is also harmonic, and, second, the random force, which acts on atoms in region 1 and originates from unknown initial positions and velocities of atoms in region 2, was assumed to be of zero mean and a stationary random process. In their method the stochastic properties of the random force were obtained applying the canonical distribution of the entire system $1\cup 2$, which was facilitated in practice by the first assumption (harmonicity of the entire system).

We have shown here that their derivation has a defect related to deriving stochastic properties of the random force from the canonical distribution of the whole system. This method is not appropriate because it leads to performing statistical averaging over dynamical variables (positions and velocities) of region 1 twice since additional averaging is assumed to be done during the course of the MD simulation of atoms in region 1. In addition, we explicitly demonstrate that this method leads to the random force, which in general does not represent a stationary random process, thereby invalidating the derivation of the Brownian form of the GLE in AD.

To cure this defect, we suggested another method in which the stochastic properties of the random force are derived from the canonical distribution of region 2, i.e., of a *subsystem* of the entire system. This allowed us to overcome eventually both difficulties of the original derivation in AD. As a bonus, we also find that it is not necessary anymore to assume that region 1 is also harmonic: it could be arbitrarily anharmonic. Still, the same GLE is obtained in which the friction kernel is essentially the random force autocorrelation function. Thus, the second dissipation-fluctuation theorem between the random force and the friction (in the general non-Markovian case) has been proven for this problem without making any additional assumptions. Note that our expression for the random force differs from that given in AD. We have also shown (using a modified method of Adelman[20]) that after the external perturbation applied to region 1 has ceased, the region relaxes to thermal equilibrium corresponding to a canonical distribution with the same temperature as in region 2. We find, however, that atoms in region 1 still feel the effect of atoms in the surrounding region 2 since atoms in the latter region instantaneously respond to the movement of atoms in region 1 resulting in an effective interaction between atoms in region 1.

Our method is based on two essential assumptions. The first one is related to assuming that region 2 can be considered in thermal equilibrium described by a canonical distribution at some temperature T. In practice, this means that the reduced distribution function for region 2,

$$\rho_2(u_2,p_2) = \int \rho(r,p,t)dr_1 dp_1,$$

where $p_1 = m_1\dot{r}_1$ and $\rho(r,p,t)$ is the distribution function of the entire system, does not longer depend on time and corresponds to the equilibrium canonical distribution (17). This assumption is justified by the very large size of region 2, and our basic assumption that only a finite fragment of the entire system (region 1) can be considered out of equilibrium.

Second, we assume that there is a *linear connection* between the two regions: their interaction energy is linear with respect to the displacements of atoms in region 2. This is a natural choice as atoms in region 2 are assumed to be far away from the local perturbation applied somewhere in the central part of region 1 (which is assumed to be large enough) and thus terms associated with higher powers of region 2 atomic displacements can be neglected. However, from the mathematical point of view, this particular assumption can in fact be relaxed. Indeed, if we keep one more term in the interaction part of the Hamiltonian (1),

$$\frac{1}{2}\sum_{j,j'\in 2} u_j^\dagger h_{jj'} u_{j'} = \frac{1}{2}u_2^\dagger h_{22} u_2,$$

which is quadratic in displacements in region 2 (the 3 × 3 matrix h_{jj}, which dimension is due to hidden Cartesian components of the displacements of atoms j and j', generally depends on positions r_1 of atoms in region 1), then the solution (6) for the harmonic region 2 would be still formally valid if we make a replacement $\Phi_{jj'} \to \Phi_{jj'} + h_{jj'}$. This would affect the definition of the matrix $\Omega_{22}(t)$ as well. Therefore, $x_2(t)$ can still be substituted into the appropriate force terms in the equations of motion for atoms in region 1 leading to an analog of Eq. (8). Unfortunately, as can easily be seen, the transparent picture of the Gaussian random force would not be valid anymore. Indeed, the extra interaction term, after employing Eq. (6) for $x_2(t)$, results in an additional force to be added on the right-hand side of the GLE (8), which is quadratic with respect to initial displacements and velocities of atoms in region 2. This means that the random force looses its linearity with these and, as a result, is not longer Gaussian. The expression for the memory term becomes also more complicated. If we retain cubic, quadric, etc. terms in the interaction part of the Hamiltonian, then an analytic solution for region 2 cannot be obtained at all and the problem becomes completely intractable. Thus, the obtained GLE [Eq. (35)] is based essentially on the particular form of the Hamiltonian for the entire system we have chosen in which the interaction term is linear with respect to the displacements of atoms in the thermal bath region.

The GLE can be easily generalized for systems containing several environments held at different temperatures, e.g., for heat transport calculations. Indeed, if we imagine a sandwichlike geometry of the entire system in which we have a central region (as region 1) and two environment regions on the left and on the right held at temperatures T_1 and T_2, then one can use Eq. (6) for the displacements in either of the regions with different matrices $\Omega_{22}(t)$. Substituting both solutions into the equation of motion for atoms in the central region 1, we obtain two random forces and two friction integral terms corresponding to each of the environment regions. In this case each of the random forces is described by its own statistics corresponding to the environment region in question. A similar in spirit method for treating heat transport in MD simulations by introducing "thermal walls" at different temperature was proposed in Ref. 24.

Finally, we shall discuss the meaning of the GLE. To simplify the argument, let us assume that we are only interested in a single set of initial positions and velocities of atoms in region 1 chosen as $r_1(0)$ and $v_1(0) = \dot{r}_1(0)$. Then, if we wanted to study a *single* trajectory of our system corresponding to some particular initial positions and velocities of atoms in region 2, we would have to draw at random $u_2(0)$ and $v_2(0) = \dot{u}_2(0)$. These would determine completely the "random" force at all times; see Eq. (14). In other words, the simulation would be entirely deterministic—as it should since it corresponds to a single trajectory in the entire phase space of the whole system. Moreover, this approach would be impractical as the number of degrees of freedom in region 2 is essentially infinite. What we would actually like to do is to sample many trajectories corresponding to various choices of positions and velocities of atoms in region 2 in a single MD simulation performed for atoms in region 1. Notice that every particular choice of the initial positions and velocities of atoms in region 2 would entail solving the same Eq. (35) but with a different force $R_1(t)$. Taking statistical average over region 2 as before of both sides of Eq. (35), we obtain an equation of motion, which corresponds to this type of the *average trajectory*,

$$m_1\langle \ddot{r}_1\rangle = \langle \widetilde{f}_1\rangle - \int_0^t \Gamma_{11}(t-\tau)\langle \dot{r}_1(\tau)\rangle d\tau \tag{55}$$

since the random force has the zero mean. Here $\langle \dot{r}_1\rangle = \frac{d}{dt}\langle r_1\rangle$ and $\langle \ddot{r}_1\rangle = \frac{d^2}{dt^2}\langle r_1\rangle$ can be written as derivatives of the average trajectory $\langle r_1\rangle$. However, there is a problem with this equation: Since $\widetilde{f}_1 = \widetilde{f}_1[r_1(t)]$ depends on the actual positions of atoms in region 1, then $\langle \widetilde{f}_1\rangle \neq \widetilde{f}_1[\langle r_1\rangle]$, i.e., the equation above cannot be written entirely via the average trajectory. The practical solution to this problem as was suggested in AD was to treat $R_1(t)$ as a random process, i.e., by choosing R_1 at each time step at random. This is easily possible since the number of degrees of freedom in region 1 (and thus, the number of random forces one has to draw to build up the vector R_1) is finite and we know the statistical properties of it. Unfortunately, there is no proof at present that the two approaches, namely that of AD and of Eq. (55), would give identical results, so that (similarly to ergodicity, which may be considered as a similar concept) the method of AD should be considered as a hypothesis.

In the next paper of this series[17] we shall derive from the GLE a simplified set of equations, which give a solid foundation for the stochastic boundary conditions method used previously without proof in some of the MD simulations.[5,25–27]

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APPENDIX

When deriving the GLE in AD [see their Eq. (4.1a)], it was assumed that the random force represents a stationary process; see Eq. (3.2) in AD. We shall show in this Appendix that if the statistical averaging is performed over the whole system $1\cup 2$ as was done in AD, then the random force becomes nonstationary hence invalidating Eq. (3.2) of AD. As a result, the Brownian form of the GLE [Eq. (4.1a) in AD] becomes unjustified as well. Note in passing that the way in which the statistical averaging is actually performed in AD is not said explicitly in the paper. However, one can figure this out since the mean of the random force defined in Eqs. (2.7b) and (2.9) in AD is assumed to be zero. This can only happen if the statistical average is performed over the entire harmonic system. We shall use our present notations in this Appendix to avoid confusion.

The random force in AD is defined without the third term in Eq. (14). Assuming the whole system $1\cup 2$ is harmonic, one can calculate the statistical averages over the whole system for the initial displacements and velocities of atoms in region 2,

$$\langle x_2(0)x_2^\dagger(0)\rangle = \frac{1}{\beta}\sum_\lambda \frac{\bar{e}_\lambda \bar{e}_\lambda^\dagger}{\bar{\omega}_\lambda^2} = \frac{1}{\beta}(\bar{D}^{-1})_{22}, \qquad (56)$$

$$\langle \dot{x}_2(0)\dot{x}_2^\dagger(0)\rangle = \frac{1}{\beta}1_{22}, \qquad (57)$$

where $\bar{D}=\begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22}\end{pmatrix}$ is the dynamical matrix for the entire system, and $\bar{e}_\lambda$ and $\bar{\omega}_\lambda^2$ are its eigenvectors and eigenvalues. Note that these should be distinguished from the analogous quantities introduced in Sec. II A and defined with respect to the dynamical matrix D_{22} of region 2 only. Consequently, the correlation function of the random force defined as in AD, i.e., without the last term in Eq. (14),

$$\begin{aligned}\langle R_1(t)R_1^\dagger(t')\rangle &= V_{12}[\dot{\Omega}_{22}(t)\langle x_2(0)x_2^\dagger(0)\rangle\dot{\Omega}_{22}(t') \\ &\quad + \Omega_{22}(t)\langle \dot{x}_2(0)\dot{x}_2^\dagger(0)\rangle\Omega_{22}(t')]V_{21} \\ &= \frac{1}{\beta}m_1^{-1/2}D_{12}[\dot{\Omega}_{22}(t)(\bar{D}^{-1})_{22}\dot{\Omega}_{22}(t') \\ &\quad + \Omega_{22}(t)\Omega_{22}(t')]D_{21}m_1^{-1/2}.\end{aligned}$$

The expression in the square brackets can be compared with Eq. (29), which does depend on the time difference $t-t'$. The difference between the two expressions is in the first term: the matrix $(\bar{D}^{-1})_{22}$ in the equation above is replaced by D_{22}^{-1} in Eq. (29). This leads to the correlation function depending on both times. To see this explicitly, let us expand the matrix $(\bar{D}^{-1})_{22}$ in a series (assuming weak interaction between two regions),

$$\begin{aligned}(\bar{D}^{-1})_{22} &= (D_{22} - D_{21}D_{11}^{-1}D_{12})^{-1} \\ &= D_{22}^{-1} + D_{22}^{-1}A_{22}D_{22}^{-1} + D_{22}^{-1}A_{22}D_{22}^{-1}A_{22}D_{22}^{-1} + \ \ldots ,\end{aligned}$$

where $A_{22}=D_{21}D_{11}^{-1}D_{12}$. The first term of the expansion leads to $\Pi_{22}(t-t')$ as in Eq. (29). However, other terms cannot be worked out into a form containing only the time difference. For instance, the second term contributes

$$\dot{\Omega}_{22}(t)(D_{22}^{-1}A_{22}D_{22}^{-1})\dot{\Omega}_{22}(t') = \Pi_{22}(t)A_{22}\Pi_{22}(t'),$$

where we have used identity (28). It depends on both times separately. In fact, summing up the whole series does not cure the problem,

$$\begin{aligned}&\dot{\Omega}_{22}(t)(\bar{D}^{-1})_{22}\dot{\Omega}_{22}(t') + \Omega_{22}(t)\Omega_{22}(t') \\ &\quad = \Pi_{22}(t-t') + \Pi_{22}(t)(A_{22}^{-1} - D_{22}^{-1})^{-1}\Pi_{22}(t').\end{aligned}$$

Alternatively, one could consider the correlation functions $\langle R_1(t)\dot{R}_1^\dagger(0)\rangle$ and $\langle \dot{R}_1(t)R_1^\dagger(0)\rangle$ explicitly only to show that these do not equal minus each other as would be the case if the random force corresponded to a stationary process contrary to Eq. (3.2) of AD.

Thus, an assumption made in AD concerning the random force in fact contradicts the explicit nature of the heat bath. As a result of this, Eq. (4.1a) remains not proven. As is shown in Sec. II B, in order for the random force to represent a stationary process, one has to perform statistical averaging using only the Hamiltonian of region 2 as averaging over the entire system leads to problems.

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