Generalized Langevin equation for solids. II. Stochastic boundary conditions for nonequilibrium molecular dynamics simulations

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The generalized Langevin equation (GLE) [L. Kantorovich, Phys. Rev. B **78**, 094304 (2008)], which describes dynamics of a finite and possibly highly anharmonic subsystem surrounded by an extended harmonic solid, is simplified here assuming short-range interactions between atoms. We show that in this case quite naturally the GLE can be worked into a form which corresponds to considering central atoms of the finite region as governed by usual Newtonian mechanics, while the boundary atoms are treated as Langevin atoms, i.e., they experience friction and random forces [the so-called stochastic boundary conditions (SBCs)]. We show that the random forces constitute a stationary Gaussian random process with the dispersion directly related to the friction coefficient in a usual way. Next, we rigorously demonstrate that, even though not all atoms are stochastic within the SBC model, the system should still arrive at canonical distribution at long times. Since the SBC model follows directly from the general GLE description and can perform as a correct *NVT* thermostat, we propose that the SBC is a method of choice if one wants to do nonequilibrium molecular dynamics simulations correctly. Our derivation of SBC is physically more acceptable than given previously when the central region atoms were assumed to be much heavier than those in the surrounding lattice (the zero-frequency approximation).

I. INTRODUCTION

In many applications such as 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] conventional molecular dynamics (MD) techniques based on *equilibrium NVT* thermostats[12–18] are normally used. This approach can only be used if the energy release within the simulated region is small as compared with the average energy of the region itself, i.e., when the dissipated energy due to some nonequilibrium process under study is relatively small and thus temperature increase of the simulated region due to this process can be neglected. However, this is not always the case, e.g., when high energy particles are impinged on a crystal surface creating a "hot spot" which causes significant local heating of the impact region with subsequent energy transfer to the bulk of the material. In such cases one cannot use MD simulations with periodic boundary conditions. However, a physically more significant problem is due to usage of MD techniques which are, strictly speaking, only applicable in thermodynamic equilibrium. The problem becomes even more difficult for the equilibrium methods when there is a gradient of temperature in the system created, e.g., by two opposite walls held at different temperatures as in heat transport experiments.

To treat this kind of problems, Adelman and Doll[2] (AD hereafter; see also Refs. 3, 4, and 19–22) proposed a generalized Langevin equation (GLE) method in which dynamics of a finite region is actually studied; however, the existence and energy transfer to or from a macroscopically large surrounding region is also accounted for within the approximation that the whole crystal is harmonic. It was shown in the previous paper of this series[23] that there is a logical inconsistency in AD which essentially invalidates their derivation

of the Brownian (or Langevin) form of the GLE. Instead, another method was proposed in Ref. 23 which is free from the problem and is also not based on assuming the region of interest to be harmonic. In fact, this region (region 1 hereafter) can be arbitrarily anharmonic. Still, it is assumed that the surrounding macroscopically large region (region 2) is harmonic and the two regions interact with each other in such a way that the corresponding interaction part of the Hamiltonian is linear in displacements u_2 of atoms in region 2.

Although region 1 can be arbitrarily anharmonic, it was also rigorously shown in Ref. 23 using the method of Ref. 24, that after the source of local heating has ceased, region 1 will arrive at thermodynamic equilibrium. The corresponding canonical distribution is based on the Hamiltonian in which atoms in the two regions interact via an effective interaction corresponding to atoms in region 2 clamped at instantaneous equilibrium positions. The latter instantly adjust to the current positions of atoms in region 1.

Although it was indicated in Ref. 23 that there is a way of implementing the method exactly, this is still very difficult. Therefore, a natural question arises of whether it is possible to make some reasonable approximations to the GLE to transform it into a more accessible technique, and not to loose all the nice physics it is based upon along the way. Here we suggest such a method: by assuming a short-range interaction between atoms (and a number of other plausible assumptions such as, e.g., Markovian approximation) we show that the GLE can be rigorously manipulated into a much simpler and actually more familiar form, in which internal atoms of region 1 move in accordance with usual Newtonian dynamics, while boundary atoms, separating the internal atoms from those in region 2, are treated as Langevin atoms. This means that the boundary atoms experience also friction and random forces, the approach we shall refer to as stochastic boundary condition (SBC) method. This way

the boundary atoms serve as a buffer: the friction forces would take the extra energy out of the "normal" atoms of region 1, while the random forces would bring the energy in by doing a work on the boundary atoms. We also derive a relationship between the dispersion of the random force and the friction coefficient, and this appears to be the same as is normally used in running Langevin dynamics.[4,25–27]

Since the SBC is an approximation, one may ask if the general behavior of the system under the SBC will be still the same as of that governed by the exact GLE. In particular, the important question is of whether or not the system will return to the thermodynamic equilibrium described by the correct canonical distribution after the source of the local perturbation has ceased. We show that this is also the case by proving a theorem: in spite of the fact that not all atoms in the simulation region (region 1) are stochastic (in fact, it would be sufficient if only one atom was stochastic), the system will arrive at the thermodynamic equilibrium, and for this to be true, exactly the same relationship between the dispersion of the friction force and the friction should hold as derived directly from the GLE. In other words, in equilibrium the energy lost through friction is to be exactly compensated by the energy influx through the stochastic forces on boundary atoms. Thus, the SBC conserves the main features of the exact consideration based on the GLE and is thus *internally consistent*.

One may go even further and assume that even in the cases of higher temperatures when region 2 cannot be considered as purely harmonic and thus the GLE is not strictly speaking applicable, one can still apply the SBC to perform nonequilibrium MD simulations on a finite region of interest. This assumption is supported by the theorem, mentioned above, that under the SBC any system will acquire canonical distribution at long enough times. It is important that the proof of this theorem given here does not depend on whether atoms in region 2 are harmonic or not.

Hence, in this paper we *derive* a simple scheme which can be used to perform MD simulations on region 1 taking into account the presence of region 2, including possible energy transfer between the two regions. Since the SBC method is consistent with GLE, at least for not very large temperatures, it may serve as a practical way of performing MD simulations in the *NVT* ensemble, both equilibrium and nonequilibrium (although the latter is more important of course, as other equilibrium MD techniques also exist).

Note that this type of MD simulations based on performing Langevin dynamics for boundary atoms of the simulation region has already been used by a number of authors,[5,28–30] although no proof has been given; it was only hinted in Ref. 30 that SBC may be derived from the GLE. Note also that the "zero-frequency" method of deriving Langevin (Brownian) dynamics from the GLE suggested previously[19] we believe is less acceptable than ours since the former method is based on a physically incorrect assumption that atoms in region 1 are much heavier than atoms in region 2.

The plan of the paper is as follows. In Sec. II we derive the SBC from the GLE. In Sec. III we consider the condition of thermodynamic equilibrium for a system governed by the SBC. Finally, the paper closes with a short discussion and conclusions.

II. DERIVATION OF SBC FROM GLE

In Sec. II A we shall briefly outline the main ideas behind the GLE and shall introduce all the necessary notations.

A. GLE

Consider an extended system consisting of atoms moving around according to the Newtonian dynamics. We split the system into two regions: a finite region 1 and the surrounding region 2. Positions of atoms in region 1, denoted by the vector column $r_1(t) = \|r_i(t)\|$, $i \in 1$ (we shall not show explicitly Cartesian components of vectors and matrices to simplify notations), are arbitrary within region 1, while atoms in region 2 oscillate about their equilibrium positions and hence we shall describe their actual positions via displacements u_j, $j \in 2$, comprising the vector column $u_2(t) = \|u_j(t)\|$. The Hamiltonian of the whole system is

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 = \mathcal{H}_1 + \left[\frac{1}{2} \sum_{j \in 2} m_j \dot{u}_j^2 + \frac{1}{2} \sum_{j,j' \in 2} u_j \Phi_{jj'} u_{j'} \right] + \sum_{j \in 2} h_j u_j, \quad (1)$$

where $\mathcal{H}_1 = T_1 + U_1$ is the Hamiltonian of atoms in finite region 1, including their kinetic, T_1, and potential, U_1, energies, the terms inside the square brackets describe the harmonic region 2 with m_j being the mass of atom $j \in 2$, $\dot{u}_j$ its velocity, and $\Phi_{jj'}$ elements of the region 2 force-constant matrix $\Phi_{22} = \|\Phi_{jj'}\|$, and the last term corresponds to the interaction between the two regions with $-h_j$ being the force with which atoms in region 1 act on atom j. This force is generally time dependent since atoms in region 1 change their positions. Note that we assume that the interaction energy is linear with respect to displacements of atoms in region 2. The dagger hereafter is used to indicate the transposed vectors and matrices.

It was shown in Ref. 23 that upon solving for displacements in region 2 and performing statistical averaging with respect to this region, the following GLE for atoms in region 1 is obtained describing their *average* trajectory:

$$m_1 \ddot{r}_1 = \tilde{f}_1 + R_1 - \int_0^t \Gamma_{11}(t,\tau) \dot{r}_1(\tau) d\tau, \quad (2)$$

where m_1 is the diagonal matrix of region 1 atomic masses. Then,

$$\tilde{f}_1 = f_1 + V_{12}(t) D_{22}^{-1} V_2(t) \quad (3)$$

is the effective force acting on atoms in region 1. In particular, f_1 is the force due to other atoms in region 1, while the second term is due to interaction with atoms in region 2 clamped at their instantaneous equilibrium positions which follow actual positions of atoms in region 1. $D_{22} = m_2^{-1/2} \Phi_{22} m_2^{-1/2}$ is the region 2 dynamical matrix with eigenvalues ω_λ^2 and eigenvectors e_λ, while m_2 is the diagonal matrix of region 2 atomic masses. The vector $V_2 = \|V_j\| = \|h_j / \sqrt{m_j}\|$ corresponds to the minus force acting on region 2 atoms, while $V_{12} = \frac{\partial V_2}{\partial r_1} = \|\frac{\partial V_j}{\partial r_i}\|$ is its derivative taken with re-

spect to positions of atoms in region 1. Since atoms in region 1 move, both the vector $V_2(t)$ and the matrix $V_{12}(t)$ are generally time dependent.

The last two terms on the right-hand side in Eq. (2) originate from vibrations of atoms in region 2. In particular, $R_1(t) = \|R_i(t)\|$ is the force due to unknown initial positions of atoms in region 2 and the last term in Eq. (2) describes friction with memory. The random force R_1 is proportional to the matrix V_{12}. Atoms in region 2 are assumed to be in thermodynamic equilibrium and thus perform as a *heat bath* described explicitly by the corresponding canonical distribution with the region 2 Hamiltonian $\mathcal{H}_2$ which contains interaction between the two regions [see Eq. (1)]. The random force is linear with respect to initial positions and velocities of region 2 atoms. Since the Hamiltonian of region 2, $\mathcal{H}_2$, is quadratic with respect to coordinates of region 2 atoms, the random force can be considered as a Gaussian stochastic process with distribution

$$P(R_1;t) \sim \exp\left(-\frac{1}{2}R_1^{\dagger}S_{11}^{-1}R_1\right), \quad (4)$$

where the dispersion matrix S_{11}, given by the equal time correlation function of the random force, is exactly proportional to the temperature ($\beta = 1/k_B T$),

$$S_{11} = \langle R_1(t)R_1^{\dagger}(t)\rangle = \frac{1}{\beta}V_{12}(t)D_{22}^{-1}V_{21}(t). \quad (5)$$

The different time correlation function of the random force,

$$\langle R_1(t)R_1^{\dagger}(t')\rangle \equiv \frac{1}{\beta}\Gamma_{11}(t,t') = \frac{1}{\beta}V_{12}(t)\Pi_{22}(t-t')V_{21}(t'), \quad (6)$$

is exactly proportional to the friction kernel in the last term in Eq. (2) (which manifests itself as a fluctuation-dissipation theorem[31]) and is related to the matrix

$$\Pi_{22}(t) = \sum_{\lambda}\frac{e_{\lambda}e_{\lambda}^{\dagger}}{\omega_{\lambda}^2}\cos(\omega_{\lambda}t). \quad (7)$$

We see that in general the random force is *not* a stationary process in exact formulation since the correlation function depends on both times, not just on their difference. However, as will be demonstrated in Sec. II B, under certain, rather plausible, assumptions it becomes the one.

B. Stochastic boundary conditions

Here we shall show, that, under the assumption of a short-ranged interaction between atoms, GLE (2) can be manipulated into a simple form which corresponds to considering only the boundary atoms by means of the Langevin (or Brownian) dynamics, the method which is referred to as the SBC. To this end, let us assume that nondiagonal elements of the dynamical matrix, $D_{kk'}$, are equal to zero if the distance between any atoms k and k' is larger than a certain critical distance. In this case we can split region 1 into two subregions C (central) and L (Langevin, see later). Region L serves as an appropriate buffer region between regions C and
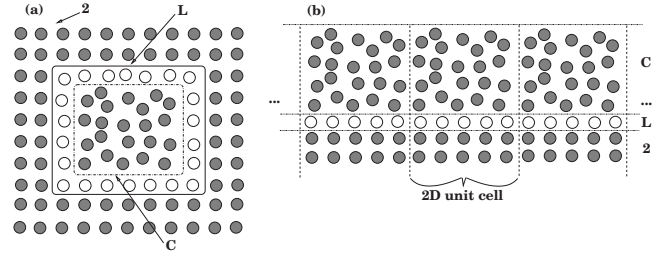

FIG. 1. Partitioning of an extended system into regions used in implementing the short-range approximation: (a) a bulk system, no periodic symmetry is present, and (b) a surface system, which has a two-dimensional (2D) periodic symmetry in the direction across the surface. Region 1 is split into two subregions: the central region C and a buffer region L separating regions C and 2. Regions L and 2 are both harmonic regions where atoms oscillate about their equilibrium positions, while atoms in region C move arbitrarily. Only atoms in region L are shown to experience friction and random forces, i.e., these are Langevin atoms.

2. Atoms in region C are allowed to move arbitrarily, while atoms in regions L oscillate about their equilibrium positions, similarly to atoms in region 2. Therefore, positions of atoms in region L will be described by the vector column of displacements $u_L = \|u_i\|$, $i \in L$. The schematic of the partitioning for a bulk and surface systems is shown in Fig. 1.

By choosing region L appropriately, we may assume that there is no interaction between atoms of regions 2 and C; however, both regions interact with atoms in the buffer region L. This explicitly means that the elements V_j ($j \in 2$) of the vector column $V_2 = \|V_j\|$ are

$$V_j = \frac{1}{\sqrt{m_j}}h_j = \frac{1}{\sqrt{m_j}}\sum_{i\in L}\Phi_{ji}u_i = \sum_{i\in L}\sqrt{m_i}D_{ji}u_i, \quad j \in 2, \quad (8)$$

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

$$V_{ij} = \frac{\partial V_j}{\partial u_i} = \begin{cases} 0 & \text{if } i \in C \\ \frac{1}{\sqrt{m_j}}\Phi_{ij} = \sqrt{m_i}D_{ij} & \text{if } i \in L. \end{cases} \quad (9)$$

Since $V_{ij} = 0$ if $i \in C$, we first see that the random force acts only on atoms from the buffer region L since $R_1(t)$ contains V_{12} as a common prefactor.[23] This means that the integral friction term is also to be applied to atoms from region L [this also follows directly from Eqs. (2) and (6)].

Finally, if we look at the definition of the effective force $\tilde{f}_1$ acting on atoms in region C [see Eq. (3)], then we notice that it is equal to f_1, i.e., this is the force due to all atoms in region $1 = C \cup L$, while the additional term $f_L^{(20)}(t) = V_{L2}D_{22}^{-1}V_2$ acts only on atoms $i \in L$ from the buffer region. Therefore, equations of motion for atoms in central region C look as in ordinary Newtonian dynamics,

$$m_i\ddot{r}_i = f_i, \quad i \in C, \quad (10)$$

while the equations of motion for atoms in the buffer region read

$$m_i \ddot{r}_i = \widetilde{f}_i + R_i - \beta \sum_{i' \in L} \int_0^t \langle R_i(t) R_{i'}^\dagger(\tau) \rangle \dot{r}_{i'}(\tau) d\tau, \quad i \in L. \tag{11}$$

The force $\widetilde{f}_i$ above, which effectively originates from the interaction of atom i with all atoms in regions 1 and 2, can be written in more detail since atoms in region L are assumed to be harmonic,

$$\widetilde{f}_L = f_L^{(C)} - \Phi_{LL} u_L + f_L^{(2_0)}(t), \tag{12}$$

where $f_L^{(C)}$ is the force on atoms $i \in L$ due to all atoms in region C, while the second term is due to harmonic atoms in region L and so it is proportional to their displacements u_L and the corresponding force-constant matrix is given by Φ_{LL}. The last term in the force $\widetilde{f}_L$ accounts for the interaction of atoms $i \in L$ with all atoms in region 2 clamped at their instantaneous equilibrium positions [see Eq. (3)],

$$f_L^{(2_0)}(t) = V_{L2} D_{22}^{-1} V_2 = \Phi_{L2} \Phi_{22}^{-1} \Phi_{2L} u_L,$$

so that the final force becomes

$$\widetilde{f}_L = f_L^{(C)} - (\Phi_{LL} - \Phi_{L2} \Phi_{22}^{-1} \Phi_{2L}) u_L = f_L^{(C)} - \widetilde{\Phi}_{LL} u_L. \tag{13}$$

This is indeed the total force acting on atoms in the buffer region due to all atoms in the system; in particular, atoms in region 2 are in equilibrium positions which dynamically change as the atoms in region L move. Note, however, that within the short-range approximation we are concerned with here, this effect may be considered as small since the corresponding contribution is of the second order with respect to the off-diagonal elements of the force-constant matrix, Φ_{L2}.

The correlation function of the random force [Eq. (6)] in the short-range approximation becomes

$$\langle R_L(t) R_L^\dagger(t') \rangle = \frac{1}{\beta} V_{L2} \Pi_{22}(t - t') V_{2L}. \tag{14}$$

Since V_{L2} does not depend on time within the short-range approximation [Eq. (9)], the correlation function now depends on the time difference. In other words, the random process within this approximation becomes stationary exactly.

At the next step, we shall assume that there is no correlation between random forces acting on different atoms of region L and that there is no dependence on the Cartesian components of the forces $\alpha, \alpha' = x, y, z$, i.e.,

$$\langle R_{i\alpha}(t) R_{i'\alpha'}(\tau) \rangle \simeq \delta_{ii'} \delta_{\alpha\alpha'} \langle R_{ix}(t) R_{ix}(\tau) \rangle, \tag{15}$$

where $i, i' \in L$. Moreover, we shall assume that the random forces R_i are statistically independent of each other so that each component of the force, $R_{i\alpha}$ ($\alpha = x, y, z$), can be drawn from its own Gaussian distribution [cf. Eq. (4)],

$$P(R_{i\alpha}) = \frac{1}{\sqrt{2\pi}\sigma_{i\alpha}} \exp\left(-\frac{R_{i\alpha}^2}{2\sigma_{i\alpha}^2}\right), \quad i \in L, \tag{16}$$

with the dispersion

$$\sigma_{i\alpha} = \langle R_{i\alpha}^2(t) \rangle = \frac{m_i}{\beta}(D_{L2} D_{22}^{-1} D_{2L})_{i\alpha,i\alpha} = \frac{1}{\beta}[V_{L2}\Pi_{22}(0)V_{2L}]_{i\alpha,i\alpha}$$

$$= \frac{1}{\beta}(\Phi_{L2}\Phi_{22}^{-1}\Phi_{2L})_{i\alpha,i\alpha}, \quad i \in L \tag{17}$$

as follows from Eqs. (5) and (9). Note that in this case the probability distribution of the random force on atom i does not anymore depend on time. In addition, the dispersion does not depend on atomic masses (only on the temperature and the interaction between atoms).

Therefore, collecting all these results, we arrive at the following equation of motion for atoms in region L:

$$m_i \ddot{r}_i = \widetilde{f}_i + R_i - \beta \int_0^t \langle R_{ix}(t) R_{ix}(\tau) \rangle \dot{r}_i(\tau) d\tau, \quad i \in L. \tag{18}$$

At the final step, we apply the Markovian approximation assuming that the correlation function of the random force decays sufficiently fast with time,

$$\dot{p}_i = \widetilde{f}_i + R_i - \gamma_i p_i, \quad i \in L, \tag{19}$$

where $p_i = m_i \dot{r}_i$ is the moment of atom i, while

$$\gamma_i = \frac{\beta}{m_i} \int_0^t \langle R_{ix}(t) R_{ix}(\tau) \rangle d\tau \Rightarrow \frac{1}{m_i} \int_0^\infty [V_{L2}\Pi_{22}(\tau)V_{2L}]_{ix,ix} d\tau \tag{20}$$

is the friction coefficient. The time integral can be calculated approximately as

$$\int_0^\infty [V_{L2}\Pi_{22}(\tau)V_{2L}]_{ix,ix} d\tau \simeq \frac{1}{2}[V_{L2}\Pi_{22}(0)V_{2L}]_{ix,ix}\delta\tau,$$

with $\delta\tau$ being a constant of the dimension of time which depends on the rate of the actual decay of the matrix $\Pi_{22}(\tau)$ with τ. The factor $\frac{1}{2}$ corresponds specifically to a linear decay of $\Pi_{22}(\tau)$ to zero over the time $\delta\tau$ and has been chosen here for convenience. Using now Eq. (17), we can relate the dispersion and the friction coefficient as follows:

$$\sigma_{i\alpha} = \frac{m_i}{\beta}\frac{2\gamma_i}{\delta\tau} = \frac{2m_i\gamma_i k_B T}{\delta\tau}. \tag{21}$$

This expression is identical to that normally used in running Langevin MD simulations[4,25–27] if $\delta\tau$ has the meaning of the MD time step. Thus, it is assumed in these simulations that the random force autocorrelation function decays over a very short time corresponding to the MD time step.

Thus, we have shown employing a number of approximations that the GLE transforms into a set of equations of motion in which atoms inside region 1 (the central region C atoms) are governed by ordinary MD equations, while the boundary atoms (in region L) move in accordance with the Langevin dynamics. In the latter case the random force $R_{i\alpha}$ is drawn at random at each time step using Gaussian distribution (16) with dispersion (17), related to the friction γ_i.

Note that another derivation of the Brownian dynamics from the GLE is also possible[19] based on expanding the friction kernel in the Fourier space around the zero frequency. This particular route in deriving the Langevin (or Brownian)

form of the GLE implies that atoms in region 1 are much heavier than those in the surrounding region 2. Our derivation presented in this section does not assume this: it is only based on restricting spatially interaction between atoms and hence is physically more acceptable.

III. THERMODYNAMIC EQUILIBRIUM IN LANGEVIN DYNAMICS

In this section we shall prove that a system described by SBC [Eqs. (10) and (19)] will arrive at thermodynamic equilibrium at long enough times which is a canonical distribution with the same temperature T as used in dispersion for the random force in Eq. (21). It is important to emphasize at this point that the theorem we are about to prove here is actually more general as it relies entirely on the equations of motion of atoms in region 1 and hence does not require to have Langevin atoms necessarily at the boundary of the simulation region. In fact, we shall prove here that for any system of atoms described by Newtonian dynamics, with all or only some (arbitrary) atoms being stochastic, the system arrives at the thermodynamic equilibrium described by the canonical distribution corresponding to the temperature used in sampling the random forces. This theorem establishes rigorous grounds for using Langevin dynamics, with all or only some of the atoms being stochastic, in *NVT* ensemble MD simulations on arbitrary systems, solid or liquid. At the same time, it justifies that MD simulations based on the SBC do not loose this important property of reaching the correct equilibrium in spite of the approximations involved in deriving them from the exact GLE.

Consider a system of N degrees of freedom ("atoms" for short) which positions and momenta are given by r_i and $p_i = m_i \dot{r}_i$, $i = 1, \ldots, N$. Let $V(r_1, \ldots, r_N)$ be the potential energy of the system depending somehow on the atomic positions. We shall assume that there are two types of atoms (i.e., degrees of freedom) in the system: M atoms are normal atoms governed by usual Newtonian dynamics, while $M_S = N - M$ atoms are Langevin atoms,

$$m_n \dot{p}_n = f_n, \quad n = 1, \ldots, M, \tag{22}$$

$$m_s \dot{p}_s = f_s - \gamma_s p_s + R_s, \quad s = 1, \ldots, M_S, \tag{23}$$

where the force $f_i = -\frac{\partial V}{\partial r_i}$. Indices n and s are to be used for normal and Langevin atoms, respectively. The random force, R_s, is Gaussian and stationary with probability (16). We may assume for generality that all dispersions and friction coefficients are different, i.e., σ_s and γ_s may depend on the atom index s.

To study system dynamics, we shall discretize the equations of motion in the usual manner by introducing the time step ϵ. Then, because of the random forces being independent at each step and between steps, this way we shall construct a discrete-time Markovian stochastic process which we shall write explicitly for all coordinates, both positions and momenta,

$$r_n^{(k)} = r_n^{(k-1)} + \frac{p_n^{(k-1)}\epsilon}{m_n}, \quad p_n^{(k)} = p_n^{(k-1)} + f_n^{(k-1)}\epsilon, \tag{24}$$

$$r_s^{(k)} = r_s^{(k-1)} + \frac{p_s^{(k-1)}\epsilon}{m_s},$$

$$p_s^{(k)} = p_s^{(k-1)} + (f_s^{(k-1)} - \gamma_s p_s^{(k-1)})\epsilon + \phi_s^{(k)}, \tag{25}$$

where the superscript in parentheses indicates the time step and $\phi_s^{(k)}$ are uncorrelated Gaussian distributed random variables with the dispersion $d_s = \sigma_s \epsilon$ (since $\phi_s \epsilon = R_s$). Note that only one equation contains the random process, all other equations are deterministic.

During the system evolution, coordinates of every atom would change along some trajectory; for instance, atom n coordinates run through the sequence $r_n \rightarrow r_n^{(1)}, r_n^{(2)}, \ldots, r_n^{(k)}$, while for its momentum we similarly have $p_n \rightarrow p_n^{(1)}, p_n^{(2)}, \ldots, p_n^{(k)}$ after k time steps. The system trajectory is defined by the initial conditions, which are expressed by the initial distribution function $\mathcal{P}[r^{(0)}p^{(0)}] \equiv \mathcal{P}[r(0), p(0)]$, and all the random forces which have been drawn to create the trajectory for each atom $s = 1, \ldots, M_S$ at every time step $l = 1, \ldots, k$. Since all random variables $\phi_s^{(k)}$ are completely independent, both in terms of atom, s, and the time step numbers, the probability for choosing the particular random forces is given by the product of the Gaussians corresponding to each of them,

$$\mathcal{P}(\{\phi_s^{(l)} : l = 1, \ldots, k; \forall s\}) = \prod_{l=1}^{k} \prod_{s=1}^{M_S} \frac{1}{\sqrt{2\pi d_s^2}} \exp\left[-\frac{1}{2d_s^2}(\phi_s^{(l)})^2\right]. \tag{26}$$

The forces on stochastic atoms determine their momenta at each time step. Since in the following, we would like to calculate the probability to have particular positions and momenta for our atoms, we should calculate the probability for the stochastic atoms to have particular momenta due to action of the stochastic forces. This can be done using the corresponding Jacobian which is given by the determinant of the matrix of derivatives: $\left\|\frac{\partial p_s^{(l)}}{\partial \phi_{s'}^{(l')}}\right\|$. One can see explicitly from the equations of motion [Eq. (25)] that this matrix has a triangular block structure with respect to the time step indices l, l' due to causality; the momenta $p_s^{(l)}$ of atoms at time step l are independent of random forces drawn during future time steps $l' > l$. Also, for the same time step, $\frac{\partial p_s^{(l)}}{\partial \phi_{s'}^{(l)}} = \delta_{ss'}$, i.e., the diagonal blocks are exactly unit matrices. This means that the Jacobian of transformation is equal to unity, and, therefore, the probability for the stochastic atoms to have their momenta along the system trajectory, $\mathcal{P}(\{p_s^{(l)} : l = 1, \ldots, k; \forall s\})$, is equal to the probability of forces [Eq. (26)], in which we should replace the forces by the momenta using equations of motion [Eq. (25)].

As we deal with the Markovian process here, the probability to find the system after k time steps in a particular point of the phase space, provided the system has gone along the particular trajectory $\{r_i \rightarrow r_i^{(1)}, r_i^{(2)}, \ldots, r_i^{(k)}; i = 1, \ldots, N\}$ and $\{p_i \rightarrow p_i^{(1)}, p_i^{(2)}, \ldots, p_i^{(k)}; i = 1, \ldots, N\}$, is given by the product of all transition probabilities for each pair of consecutive time steps, i.e.,

$$\mathcal{P}(r^{(1)}, \ldots, r^{(k)}; p^{(1)}, \ldots, p^{(k)})$$
$$= W(r^{(k)}, p^{(k)} | r^{(k-1)}, p^{(k-1)})$$
$$\times \mathcal{P}(r^{(1)}, \ldots, r^{(k-1)}; p^{(1)}, \ldots, p^{(k-1)})$$
$$= W(r^{(k)}, p^{(k)} | r^{(k-1)}, p^{(k-1)}) \ldots$$
$$\times W(r^{(2)}, p^{(2)} | r^{(1)}, p^{(1)}) \mathcal{P}(r^{(0)}; p^{(0)}), \qquad (27)$$

where $r^{(l)} = \{r_1^{(l)}, r_2^{(l)}, \ldots, r_N^{(l)}\}$ and $p^{(l)} = \{p_1^{(l)}, p_2^{(l)}, \ldots, p_N^{(l)}\}$ are coordinates and momenta of all atoms at time step l and

$$W(r', p' | r, p)$$
$$= \left[\prod_{j=1}^{N} \delta\left(r_j' - r_j - \frac{\epsilon}{m_j} p_j \right) \right] \prod_n \delta(p_n' - p_n - f_n \epsilon)$$
$$\times \prod_s \frac{1}{\sqrt{2\pi d_s^2}} \exp\left\{ -\frac{1}{2 d_s^2} [p_s' - p_s(1 - \gamma_s \epsilon) - f_s \epsilon]^2 \right\}$$
$$\qquad (28)$$

is the corresponding transition probability of the elementary process $\{r, p\} \rightarrow \{r', p'\}$. Here we have not shown the indices of the particular time steps for simplicity of notations according to a simple agreement we shall adopt from now on: non-primed quantities correspond to the previous time step t, while primed to the next one, $t' = t + \epsilon$. Delta function terms in the expression above take care of the deterministic variables which do not directly depend on the stochastic forces; these are positions of all atoms and momenta of normal atoms. To calculate the probability $\mathcal{P}(r'; p')$ for the system to arrive at the phase-space point (r', p') via *any* route, one has to integrate over all the variables (coordinates and momenta) corresponding to time steps preceding the final one, in which case one writes the recurrence relation between such probabilities at adjacent times as follows:

$$\mathcal{P}(r'; p') = \int dr \int dp \, W(r', p' | r, p) \mathcal{P}(r; p). \qquad (29)$$

Once the transition probability has been derived, one can study the dynamics of the system probability distribution in time. However, we set for ourselves here a much more modest objective which is to obtain the system distribution function at long enough times, i.e., the stationary distribution which does not depend on time anymore. In particular, we would like to find the dispersion of the random forces distribution, d_s, which would guarantee the system to arrive at *canonical* distribution of some predefined temperature T. To this end, we assume that at some time step the system, described by the coordinates r and momenta p, satisfies the canonical distribution of temperature T,

$$\mathcal{P}_0(r; p) = \frac{1}{Z_V} e^{-\beta V(r)} \prod_{j=1}^{N} \sqrt{\frac{\beta}{2\pi m_j}} e^{-\beta p_j^2 / 2 m_j}, \qquad (30)$$

where Z_V is the coordinate part of the partition function, while its momentum part has been written above explicitly. The distribution at the next time step, characterized by coordinates and momenta r' and p', respectively, will then satisfy recurrence relation (29) in which the distribution in the inte-

grand on the right-hand side is $\mathcal{P}(r; p) \equiv \mathcal{P}_0(r; p)$.

Let us calculate the distribution function $\mathcal{P}(r'; p')$ by integrating canonical distribution (30) with transition rate (28) in formula (29). We shall perform the integration with respect to r first. Because of the delta functions in the transition probability, this simply results in the substitution $r_j \rightarrow r_j' - \frac{\epsilon}{m_j} p_j$ in the potential-energy term whereby making it dependent on the atomic momenta p_j. We expand the potential energy,

$$V\left(\left\{ r_j' - \frac{\epsilon}{m_j} p_j \right\} \right) = V(r') + \sum_{j=1}^{N} f_j' p_j \frac{\epsilon}{m_j} + O(\epsilon^2),$$

where $f_j' = -(\frac{\partial V(r)}{\partial r})_{r=r'}$ is the force acting on atom j at time t', and then integrate over momenta of all normal and stochastic atoms. The calculation is simple although slightly cumbersome. It yields

$$\mathcal{P}(r'; p') = \frac{e^{-\beta V(r')}}{Z_V} \mathcal{P}_n(\{p_n\}) \mathcal{P}_s(\{p_s\}), \qquad (31)$$

where distributions of momenta for normal and stochastic atoms are, respectively,

$$\mathcal{P}_n(\{p_n\}) = \prod_{n=1}^{M} \sqrt{\frac{\beta}{2\pi m_n}}$$
$$\times \exp\left\{ -\frac{\beta}{2 m_n} [(p_n')^2 + 2\epsilon p_n'(f_n' - f_n) + O(\epsilon^2)] \right\}, \qquad (32)$$

$$\mathcal{P}_s(\{p_s\}) = \prod_{s=1}^{M_S} \frac{1}{\sqrt{2\pi \kappa_s^2}} \exp\left\{ -\frac{1}{2 \kappa_s^2} [p_s' + (f_s' - f_s)\epsilon + O(\epsilon^2)]^2 \right\}, \qquad (33)$$

and we have introduced the following notation:

$$\kappa_s^2 = d_s^2 + \frac{m_s}{\beta}(1 - \gamma_s \epsilon)^2. \qquad (34)$$

The r'-dependent part of the distribution at time t' in Eq. (31) is exactly the same as required by the Gibbs canonical distribution. It order for the whole expression to be truly canonical, the following two factors in Eq. (31) describing momenta distributions of normal and stochastic atoms should be of the Maxwellian form. Since the difference in the forces calculated at two adjacent time steps t and t' is of the first order in ϵ, i.e., $f_j' = f_j + O(\epsilon)$, the terms with the difference of forces in the exponentials of both momenta distributions above are, in fact, of the second order in ϵ. Dropping all second-order terms, we see that the distribution of momenta of normal atoms [Eq. (32)] immediately acquires exactly the required Maxwellian form. The momenta distribution of stochastic atoms [Eq. (33)] would become the one if only $\kappa_s^2 = \frac{m_s}{\beta}$. Using Eq. (34), one finds, to the first order in ϵ, that the dispersion d_s^2 must satisfy the following relationship: $d_s^2 = 2 m_s \gamma_s \epsilon / \beta$. Therefore, we shall obtain for the dispersion of the random force, $\sigma_s^2 = d_s^2 / \epsilon^2$, exactly the same expression (21) as in Sec. II B. Thus, we have proven that in order for a

system of atoms, containing an arbitrary subsystem of Langevin atoms, to reach thermodynamic equilibrium corresponding to the correct Gibbs canonical distribution, the dispersions of the random forces should be related to the friction coefficients in the same way as derived from the GLE.

IV. DISCUSSION AND CONCLUSIONS

In this paper we have derived a simplified version of the GLE, the method which is referred to as SBC. This has been done assuming interaction between atoms has a certain range (the short-range approximation). This method is concerned with treating dynamics of an extended system by means of a finite subsystem (region 1) which in turn is split into two subregions: *C* and *L*. Region *C* atoms are governed by ordinary Newtonian dynamics due to forces from all other atoms, while region *L* atoms acquire in addition friction and random forces. The latter are shown to represent a *stationary* stochastic process which is Gaussian distributed with dispersion directly related to the friction coefficient of the friction force in the usual way.[4,25–27] Region *L* separates region *C* from the rest of the system (which is not considered explicitly) and serves as a buffer controlling the heat flow between them. This paper should serve as a solid foundation for a number of approaches[5,28–30] which were proposed earlier on intuitive grounds. In a certain sense, SBC could be considered as an *embedding* for classical MD simulations.

Note that the method of deriving Langevin (Brownian) dynamics from the GLE suggested previously[19] we believe is physically less acceptable than ours since the former method is based on assuming that atoms in region 1 are much heavier than atoms in region 2 (zero-frequency approximation). We have also proven an important theorem stating that any system of atoms containing at least one stochastic (or Langevin) atom will necessarily arrive at long enough times at thermal equilibrium corresponding to the Gibbs canonical distribution. This fact has important implications. Indeed, it was shown in Ref. 23 that a system described by the exact GLE should acquire thermal equilibrium corresponding to the canonical distribution. Since the SBC equations represent a simplified version of the GLE and thus may loose this important property of thermal equilibrium due to the nature of the approximations made, the theorem actually guarantees that this is not the case, and the SBC presents an *internally consistent* scheme capable of reaching the correct equilibrium. This fact may be used to justify the use of the SBC for a wider class of systems for which the GLE derived in Ref. 23 is not strictly applicable, e.g., solids at high temperatures or even liquids. However, the found relationship between the SBC and the GLE suggests which atoms in the simulation box are to be treated as stochastic: it follows from the GLE that these should be the boundary atoms.

Another important implication is that, since the SBC method was derived from the GLE, this must be the method of choice in running MD simulations of *nonequilibrium* processes. Note that usually employed methods based on Nose thermostat[12–18] have been derived for treating *NVT* ensembles in thermal equilibrium and, strictly speaking, are not applicable to nonequilibrium situations. In particular, SBC is a natural method in applying to situations in which there is a temperature gradient, e.g., for heat transport MD calculations. In this case the MD calculation would involve having two stochastic boundary regions separating the central region from either of the environment regions, held at different temperatures, and the dispersions of the Gaussian distributions used to draw the random force for each of the boundaries would be different due to different temperatures. A similar in spirit method for treating heat transport in MD simulations by introducing "thermal walls" at different temperatures was proposed in Ref. 32.

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