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Exact Generalized Langevin Equation for a Particle in a Harmonic Lattice*

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Projection-operator techniques are used to obtain a new exact equation for the momentum of a particle in a harmonic lattice. The equation, valid for all times and mass ratios, permits a simple physical interpretation in terms of a reference system with the particle held fixed. It is demonstrated that the random forces which arise through the use of two different projection operators are equal and identical to the force on the heavy particle in the reference mechanical system.

I. INTRODUCTION

In recent years projection-operator techniques have been widely used to develop a molecular theory of Brownian motion.[1-4] Attention is focused on deriving the Langevin equation

$$\dot{P}(t) = \zeta P(t) + E(t) \; . \tag{1}$$

This phenomenological equation describes the momentum $P(t)$ of a heavy particle in fluid bath. In it, ζ is the friction constant and $E(t)$ a random force whose stochastic properties are specified. Early efforts[5-8] to examine the molecular basis of the Langevin equation were concerned with the exact analysis of the dynamical motion of a heavy particle in a harmonic lattice.

In the projection-operator method one arrives at a generalized Langevin equation that resembles Eq. (1) and involves a complicated "random" force $F^*(t)$. For realistic systems little is known about the nature of $F^*(t)$, and approximations are required for this quantity if one is to obtain the Langevin equation. In order to assess the approximation of recent projection-operator methods[9] that have been employed for systems with general interactions, we have used these methods to examine the harmonic lattice model. The motivation for adopting this model is that explicit calculations may be performed that are not possible for more realistic systems.

The revival of interest in Brownian motion is based on recent developments[2] that use projection-operator methods to obtain generalized Langevin equations to describe a much wider class of relaxation phenomena. Our results have implications for these more general treatments as well.

II. MODEL

The Hamiltonian for the harmonic system consisting of N bath particles of mass m and one particle of different mass M is

$$H = H_0 + P_0^2/2M \; , \tag{2}$$

where

$$H_0 = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \sum_{i,j=0}^{N} \frac{1}{2} q_i A_{ij} q_j \; . \tag{3}$$

Here P_0 is the momentum of the particle of mass M (designated the zeroth particle), q_i is the deviation of particle i from its equilibrium position, and A_{ij} is the real symmetric matrix chosen to satisfy the stability condition

$$\sum_{i=0}^{N} A_{ij} = 0. \tag{4}$$

The Liouville operator of the system is

$$iL = iL_0 + iL_1 \; ,$$

where

$$iL_0 = \sum_{j=1}^{N} \left(\frac{p_j}{m} \frac{\partial}{\partial q_j} + F_j \frac{\partial}{\partial p_j} \right) , \tag{5}$$

$$iL_1 = \frac{p_0}{M} \frac{\partial}{\partial q_0} + F_0 \frac{\partial}{\partial p_0} \; . \tag{6}$$

Here F_j is the force on particle j given by

$$F_j = \frac{-\partial H}{\partial q_j} = - \sum_{l=0}^{N} A_{jl} q_l \; . \tag{7}$$

In order to compute the momentum of the force on the zeroth particle at time t,

$$\dot{P}_0(t) = e^{iLt} \dot{P}_0(0) = F_0(t) \; , \tag{8}$$

we shall make use of the operator identity

$$e^{i(A+B)t} = e^{iAt} + \int_0^t d\tau \, e^{i(A+B)(t-\tau)} iB \, e^{iA\tau} \; . \tag{9}$$

We make the identification $A+B=L$, $A=(1-\mathcal{P})L$, where $\mathcal{P}$ is a projection operator and operate with Eq. (9) on $\dot{P}_0(0)$ to obtain

$$\dot{P}_0(t)=F_0^+(t)+\int_0^t d\tau\, e^{iL(t-\tau)}\, i\mathcal{P}L F_0^+(\tau) . \qquad (10)$$

Here $F_0^+(t)$ is the "random" force defined by

$$F_0^+(t)\equiv e^{i(1-\mathcal{P})Lt}F_0(0) . \qquad (11)$$

With the choice of projection operator

$$\mathcal{P}(\cdots)\equiv\langle\cdots\rangle\equiv\frac{\int e^{-\beta H_0}\cdots dq^N dp^N}{\int e^{-\beta H_0}dq^N dp^N} \qquad (12)$$

it may easily be verified that

$$\mathcal{P}iL_0=0. \qquad (13)$$

Equation (10) reduces to the equation

$$\dot{P}_0(t)=F_0^+(t)+\int_0^t d\tau\, e^{iL(t-\tau)}\left(\nabla_{P_0}-\frac{\beta}{M}P_0\right)\times\langle F_0^+(\tau)F_0(0)\rangle , \qquad (14)$$

with use of Eqs. (13) and (6), and the fact that

$$\nabla_{q_0}\langle F_0^+(t)\rangle=\langle\nabla_{q_0}F_0^+(t)\rangle+\beta\langle F_0F_0^+(t)\rangle=0 \qquad (15)$$

since $\langle F_0^+(\tau)\rangle=0$.

The equation of motion for $P_0(t)$, Eq. (14), is an exact equation which is independent of the harmonic model. Its validity depends upon the definition of the projection operator, the fact that $\langle F^+(t)\rangle=0$, and Eq. (13). In order to proceed one must consider the properties of the random force $F^+(t)$. For systems with realistic interactions it has not proven possible to say anything in detail about the fluctuating force. However, in the harmonic model it is possible to relate $F^+(t)$ rigorously to a physically understandable mechancial force in a reference system.

Other choices for the projection operator are possible. Mori[2] has suggested a different projection operator,

$$\mathcal{P}_M(\cdots)\equiv P_0\frac{\langle\langle P_0\cdots\rangle\rangle}{\langle\langle P_0^2\rangle\rangle} , \qquad (16)$$

where the double angular bracket defines the average

$$\langle\langle\cdots\rangle\rangle=\frac{\int e^{-\beta H}(\cdots)dq^N dp^N dq_0 dp_0}{\int e^{-\beta H}dq^N dp^N dq_0 dp_0} . \qquad (17)$$

For this projection operator $\mathcal{P}_M iL_0=0$ and $\langle F_0^*(t)\rangle=0$, where $F_0^*(t)$ is the "random" force defined by

$$F_0^*(t)=e^{i(1-\mathcal{P}_M)Lt}F_0(0) . \qquad (18)$$

This definition of the projection operator leads to an exact equation of motion of the form

$$\dot{P}_0(t)=F_0^*(t)-\int_0^t d\tau\, P_0(t-\tau)\frac{\beta}{M}\,\langle\langle F_0^*(\tau)F_0(0)\rangle\rangle . \qquad (19)$$

III. EVALUATION OF RANDOM FORCE

We shall relate the "random" forces $F_0^+(t)$ and $F_0^*(t)$ to a mechanical force in a reference system. In the reference system, specified by H_0, the zeroth particle is held *fixed* while the N bath particles are permitted to move in the field of the fixed zeroth particle. The force experienced by the zeroth particle in the reference system is

$$F_0^0(t)=e^{iL_0t}F_0(0) , \qquad (20)$$

where iL_0, defined in Eq. (5), is the Liouville operator corresponding to H_0. We use Eq. (9) with the choice $A+B=(1-\mathcal{P})L$ and $A=L_0$ to relate $F_0^0(t)$ to $F_0^+(t)$. Operating on $F_0(0)$ gives us

$$F_0^+(t)=F_0^0(t)+\int_0^t d\tau\, e^{i(1-\mathcal{P})L(t-\tau)}i(1-\mathcal{P})L_1F_0^0(\tau) . \qquad (21)$$

To proceed, we evaluate $F_0^0(\tau)$. Since iL_0 describes the motion of the bath particles relative to the zeroth particle held fixed at an arbitrary position q_0, it is useful to change coordinates to

$$\hat{q}_j=q_j-q_0,\quad \hat{p}_j=p_j,\quad j=1,2,\ldots,N . \qquad (22)$$

In this coordinate system

$$F_j(0)=-\sum_{l=1}^N A_{jl}\hat{q}_l(0),\quad j=0,1,\ldots,N \qquad (23)$$

and hence iL_0 does not depend on q_0. It follows that

$$F_0^0(t)=-\sum_{l=1}^N A_{0l}\hat{q}_l^0(t) , \qquad (24)$$

where

$$\hat{q}_l^0(t)=e^{iL_0t}\hat{q}_l^0(0) . \qquad (25)$$

The $\hat{q}_l^0(t)$ may be computed using the standard normal mode analysis for harmonic lattices. The result is

$$\hat{q}_l^0(t)=\sum_{j=1}^N[C_{lj}(t)\hat{q}_j(0)+D_{lj}(t)p_j(0)], \qquad (26)$$

where $C_{lj}(t)$ and $D_{lj}(t)$ are related to the normal modes of the N-particle system. Consequently $F_0^0(t)$ may be written as

$$F_0^0(t)=-\sum_{l=1}^N A_{0l}\sum_{j=1}^N\{C_{lj}(t)[q_j(0)-q_0]+D_{lj}(t)p_j(0)\} , \qquad (27)$$

where we have made use of Eq. (22). If H_0 is transformed according to Eq. (22) it may easily be shown that $\langle\hat{q}_j\rangle=0$. It follows that $\langle q_j(0)\rangle=q_0$ and that $\langle F_0^0(t)\rangle=0$.

From the definition of iL_1 [Eq. (6)] and Eq. (27), it is easy to see that $iL_1F_0^0(t)$ yields an expression that is independent of the coordinates $q_j(0)$ and $p_j(0)$, $j=1,\ldots,N$. Therefore we have

$$(1-\mathcal{P})\,iL_1F_0^0(t)=0, \tag{28}$$

and from Eq. (21) we arrive at the important result

$$F_0^+(t)=F_0^0(t)\ . \tag{29}$$

The "random" force is identical to the force on the zeroth particle in the reference system. This simplification is realized in the harmonic lattice because the coordinates at time t are linear in the initial coordinates and momenta.

Had we chosen the Mori projection operator [Eq. (16)] we would have arrived at an equation analogous to Eq. (21):

$$F_0^*(t)=F_0^0(t)+\int_0^t d\tau\, e^{i(1-\mathcal{P}_M)L(t-\tau)}\,i(1-\mathcal{P}_M)\,L_1F_0^0(\tau)\ . \tag{30}$$

Using Eqs. (6) and (27) once more, we see that $iL_1F_0^0(\tau)$ is proportional to P_0. Consequently, using the definition of $\mathcal{P}_M$ [Eq. (16)]

$$(1-\mathcal{P}_M)\,iL_1F_0^0(t)=0, \tag{31}$$

we find

$$F_0^*(t)=F_0^0(t)\ . \tag{32}$$

The equivalence of Eqs. (14) and (19) can now be established by noting from Eq. (27) that $\langle F_0^0(\tau)F_0(0)\rangle$ is independent of P_0 and q_0 and therefore

$$\langle F_0^0(\tau)F_0^0\rangle=\langle\langle F_0^0(\tau)F_0^0\rangle\rangle. \tag{33}$$

We may now write Eq. (14) as

$$\dot P_0(t)=F_0^0(t)-\frac{\beta}{M}\int_0^t d\tau\,P_0(t-\tau)\,\langle F_0^0(\tau)F_0(0)\rangle\ . \tag{34}$$

This expression is an exact equation of motion for the zeroth particle, in which the "random" force is a simple mechanical force in the reference system of N bath particles and one fixed particle. Notice that this expression is derived without reference to the mass ratio of the zeroth particle to the bath particles and is, in fact, exact for all mass ratios.

IV. MANY-PARTICLE MODEL

Two (or more) particles of mass M separated by variable distances in a harmonic lattice may serve as an important model for a variety of hydrodynamic and radiation field problems. Our considerations may be extended to this case, once again leading to exact equations where the terms that appear have an immediate physical interpretation. For example, in the case of two particles of mass M at 0 and l in a harmonic lattice of N particles of mass m, the exact equations of motion are

$$\dot P_\alpha(t)=\langle F_\alpha\rangle(t)+K_\alpha^0(t)-\frac{\beta}{M}\int_0^t d\tau\,e^{iL(t-\tau)}\times\sum_{\beta=0,l}P_\beta(0)\langle K_\beta(0)K_\alpha^0(\tau)\rangle\ , \tag{35}$$

where

$$\alpha,\beta=0,l,\quad \langle F_\alpha\rangle(t)\equiv e^{iLt}\langle F_\alpha\rangle\ , \tag{36}$$

and

$$K_\alpha^0(t)\equiv e^{iL_0t}\,[F_\alpha-\langle F_\alpha\rangle]. \tag{37}$$

The canonical average is with respect to the Hamiltonian of the bath particles with the two Brownian particles held fixed, and iL_0 is the Liouville operator corresponding to this Hamiltonian.[10]

V. CONCLUDING REMARKS

The important results we find from our analysis are the following:

(i) The exact equation of motion for the momentum of the zeroth particle of mass M in a harmonic lattice is

$$\dot P_0(t)=F_0^0(t)-\frac{\beta}{M}\int_0^t d\tau\,P_0(t-\tau)\langle F_0^0(\tau)F_0(0)\rangle\ . \tag{38}$$

To our knowledge, previous workers have not arrived at this representation of the exact dynamics. The representation is of interest because of the simple interpretation of the "random" force $F_0^0(t)$. For nearest-neighbor interactions, it is possible to show that $\langle\langle P_0P_0(t)\rangle\rangle$ is equal to the exact result of Rubin.[4] It should be emphasized that this equation is independent of mass ratio (m/M) and may be easily extended to many dimensions, to more complicated mass distributions, and to quantum systems. We have not been able to arrive at a correspondingly simple exact Fokker-Planck equation for the distribution function of the Brownian particle in a harmonic lattice.

(ii) For the harmonic system, the "random" forces $F_0^+(t)$ and $F_0^*(t)$ are exactly equal to $F_0^0(t)$. This identical behavior for $F_0^*(t)$ and $F_0^+(t)$ need not be expected for systems with more general interactions. This is the first case where it has proven possible to interpret the "random" force, containing a modified propagator, exactly in terms of a reference mechanical system.

(iii) For general fluid systems, it is believed that $\langle F_0^+(t)F_0(0)\rangle$ approaches $\langle F_0^0(t)\,F_0(0)\rangle$ for all times as the mass ratio (m/M) becomes small. This point has recently been examined in detail by Oppenheim and Mazur.[9] For the harmonic model, these two correlation functions are exactly equal independently of mass ratio.

Quadratic Hamiltonians are used to describe relaxation for a variety of physical problems. We expect the projection-operator method will provide an economical way to arrive at exact equations which allow a direct physical interpretation of all terms without the presence of complicated modified propagators present in the projection-operator analysis of more realistic systems.

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Thermomagnetic Force in Polyatomic Gases*

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A force has been observed on a small thin disk which is immersed in a polyatomic gas when a thermal gradient is established and when a magnetic field is applied. This thermomagnetic force is normal to the surface of the disk and is an even function of the magnetic field. Measurements are reported of this force effect as a function of magnetic field and pressure for O_2 and NO in the temperature range 30–35 °C. These new results are compared to a related thermomagnetic effect on the thermal conductivity of a polyatomic gas (Senftleben-Beenakker effect).

I. INTRODUCTION

It has been known for forty years that a magnetic field could influence the transport properties of some gases. The first observation of such an influence was made when it was discovered that a magnetic field causes a decrease in the thermal conductivity of oxygen.[1] Two years later it was discovered that a magnetic field also causes a decrease in the shear viscosity of oxygen.[2] These effects in O_2 were later observed in NO and were extensively studied. It was observed that the transport coefficients decrease in a magnetic field H, that the effect is an even function of H, and that the effect approaches saturation as a function of field divided by pressure H/P.

All of the measurements can be explained qualitatively in terms of a model in which a rotating diatomic molecule of O_2 is considered as a disk with a magnetic moment in the direction of the axis of rotation.[3,4] Each disk clearly has a lower probability of a collision when moving in its own plane than when moving perpendicular to it; equivalently, a disk has a lower collision probability when the velocity and the rotational angular momentum vectors are perpendicular than when they are parallel. In the absence of an external magnetic field this causes no observable asymmetry in the properties of the gas because the velocities and angular momenta are randomly oriented and the asymmetries are averaged out. When a magnetic field is applied the averaging out is partially destroyed by the precession of the angular momenta about the field. The way this leads to a change in measurable properties of the gas can easily be imagined, for example, by picturing a molecule whose angular momentum and magnetic moment are perpendicular to the field. If the field and the magnetic moment are large enough to cause substantial precession between collisions, the disk presents a more nearly spherical collision cross section and the possibility of relatively unimpeded motion in the plane of the disk is lost. Upon averaging over all orientations of velocity and angular momentum of the molecules, the result is that the change in collision cross section causes, on the whole, a reduction in the thermal conductivity and the viscosity. Since these effects were thought to be only properties of strongly paramagnetic gases (the only ones studied) and since the Gorter[3] model explained the measurements reasonably well, interest diminished.