

Generalized Langevin Equations with Time-Dependent Temperature

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A generalized Langevin equation describing the evolution of a particle in a heat bath with a time-dependent temperature is derived for a simple model. The temperature is controlled by introducing dissipative terms in the dynamical equations of the heat bath particles. The Langevin equation contains a term that is specifically associated with the variation of the temperature.

KEY WORDS: Langevin equations; time-dependent temperature; heating and cooling processes.

1. INTRODUCTION

In recent years, mesoscopic equations have been used to describe a variety of systems with a time-dependent temperature. This approach has proved to be useful to study, for instance, the evolution of a system under continuous cooling or heating. In particular, several models for the dynamics of glasses have been formulated in this way.⁽¹⁾

Almost without exception, in most of the models it is assumed that the equation describing the time evolution of the system at constant temperature also holds when the temperature changes in time. One simply has to formally replace in the equation the constant value by the given function.

The purpose of this paper is the derivation of a Langevin equation describing the motion of a system interacting with a heat bath whose temperature changes in time, although the functional form of its distribution function is always that of equilibrium. Microscopic derivations of

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Langevin equations for systems coupled to a heat bath have been the subject of extensive work, and a great deal is now known about Brownian motion at constant temperature. However, it seems that the case of a changing temperature has not been much explored, and therefore the study of simple examples like the one presented here may be useful.

Our work is rooted in a derivation due to Zwanzig^(2,3) of nonlinear Langevin equations. Zwanzig's work is particularly interesting because it holds for arbitrary nonlinear systems. His assumptions refer to the heat bath and to the interactions between the system and the heat bath, although they are sufficiently general to allow for the derivation of Langevin equations with both additive and multiplicative noises.⁽⁴⁾

The approximation we will follow here can be applied to the whole class of models considered by Zwanzig,⁽²⁾ but for the sake of simplicity we will restrict ourselves to a specific system that was also discussed by Zwanzig to illustrate his formal results.

2. DESCRIPTION OF THE MODEL

Let us first present the model as it was formulated by Zwanzig for the case of constant temperature. We consider a particle interacting with a bath of N harmonic oscillators and subject to a potential $U(Q)$, where Q represents the position of the particle. The mass and the momentum of the particle are denoted by M and P , respectively. The position and the momentum of the j th oscillator are q_j and p_j , and its frequency is ω_j . The Hamiltonian of the system is assumed to be of the form

$$H(Q, P, \{q_j\}, \{p_j\}) = H_s(Q, P) + H_b(Q, \{q_j\}, \{p_j\}) \quad (1)$$

where

$$H_s(Q, P) = \frac{P^2}{2M} + U(Q) \quad (2)$$

is the Hamiltonian of the isolated particle, and

$$H_b(Q, \{q_j\}, \{p_j\}) = \sum_j \frac{1}{2} p_j^2 + \sum_j \frac{1}{2} \omega_j^2 \left(q_j - \gamma_j \frac{Q}{\omega_j^2} \right)^2 \quad (3)$$

is the sum of the bath and interaction Hamiltonians. The parameters γ_j characterize the coupling between the system particle and the bath of oscillators.

The above Hamiltonian leads to the following dynamical equations for the position and momentum of the particle:

$$M \frac{dQ(t)}{dt} = P(t) \quad (4)$$

$$\frac{dP(t)}{dt} = -U'(Q(t)) + \sum_j \gamma_j \left(q_j(t) - \gamma_j \frac{Q(t)}{\omega_j^2} \right) \quad (5)$$

while the corresponding equations of motion for the heat bath are

$$\frac{d}{dt} q_j(t) = p_j(t) \quad (6)$$

$$\frac{d}{dt} p_j(t) = -\omega_j^2 \left(q_j(t) - \gamma_j \frac{Q(t)}{\omega_j^2} \right) \quad (7)$$

By formally solving Eqs. (6) and (7) and introducing the result into Eq. (5), Zwanzig⁽²⁾ was able to derive an exact generalized Langevin equation for the motion of the particle. Furthermore, the equation becomes approximately Markovian in a well-defined limit. Moreover, for $N \rightarrow \infty$ the effect of the particle on the distribution function of the oscillators becomes negligible. Therefore, if one assumes that the bath was initially at equilibrium with a given temperature, this temperature remains well defined and constant along the evolution of the system. This follows directly from the fact that the canonical distribution with constant temperature is a stationary solution of the Liouville equation of the isolated bath, which corresponds to make $\gamma_j = 0$ in Eqs. (6) and (7).

If one wants the bath to have a time-dependent temperature, it is clear that one has to modify its evolution equations. The energy cannot be a constant of motion when the interactions with the particle are neglected.

Let us consider the bath in the absence of the system particle. We assume that the position and momentum of the j th bath particle obey the equations

$$\frac{d}{dt} q_j = p_j + \alpha(t) q_j \quad (8)$$

$$\frac{d}{dt} p_j = -\omega_j^2 q_j + \beta(t) p_j \quad (9)$$

where $\alpha(t)$ and $\beta(t)$ are time-dependent parameters to be determined later.

Equations (8) and (9) deserve some comments. It is easily seen that they cannot be derived from a Hamiltonian, except for the particular case

$\alpha(t) = -\beta(t)$. Our point of view is that they are the effective dissipative equations of the bath when its temperature is controlled by some kind of external mechanism. Of course, they are not the only possible choice, although they seem to be the simplest one. In the Appendix it is shown how the same effect can be obtained by means of a time-dependent Hamiltonian, but the equations are much more complicated. More will be said about this point at the end of the paper.

To determine $\alpha(t)$ and $\beta(t)$, we will use the evolution equation for the distribution function of a system of particles that obey Eqs. (8) and (9). Taking into account that they do not interact, we can restrict ourselves to the one-particle distribution function defined as

$$f(q_j, p_j, t) = \langle \delta(q_j - q_j(t)) \delta(p_j - p_j(t)) \rangle \quad (10)$$

Here the angular brackets denote average with a given probability distribution for $q_j(0)$ and $p_j(0)$. Use of Eqs. (8) and (9) leads to

$$\begin{aligned} \frac{\partial}{\partial t} f(q_j, p_j, t) = & -p_j \frac{\partial}{\partial q_j} f(q_j, p_j, t) + \omega_j^2 q_j \frac{\partial}{\partial p_j} f(q_j, p_j, t) \\ & - \alpha(t) \frac{\partial}{\partial q_j} (q_j f(q_j, p_j, t)) - \beta(t) \frac{\partial}{\partial p_j} (p_j f(q_j, p_j, t)) \end{aligned} \quad (11)$$

We want to choose $\alpha(t)$ and $\beta(t)$ in such a way that Eq. (11) admits as a time-dependent solution

$$f_0(q_j, p_j, t) = \frac{\omega_j}{2\pi k_B T(t)} \exp \left[-\frac{1}{2k_B T(t)} (p_j^2 + \omega_j^2 q_j^2) \right] \quad (12)$$

where k_B is the Boltzmann constant and $T(t)$ is a given function of t . Substitution of Eq. (12) into Eq. (11) yields

$$\begin{aligned} & \left[\frac{1}{2k_B T} (p_j^2 + \omega_j^2 q_j^2) - 1 \right] \frac{d}{dt} \ln T \\ & = \alpha(t) \left(\frac{\omega_j^2 q_j^2}{k_B T} - 1 \right) + \beta(t) \left(\frac{p_j^2}{k_B T} - 1 \right) \end{aligned} \quad (13)$$

This relation becomes an identity for

$$\alpha(t) = \beta(t) = \frac{1}{2} \frac{d}{dt} \ln T(t) \quad (14)$$

Our model can already be fully specified. We consider a particle in a

bath. The evolution equations of the particle are given by Eqs. (4) and (5), and those for the bath are

$$\frac{d}{dt} q_j = p_j + \alpha(t) q_j \tag{15}$$

$$\frac{d}{dt} p_j = -\omega_j^2 \left(q_j - \gamma_j \frac{Q}{\omega_j^2} \right) + \alpha(t) p_j \tag{16}$$

where $\alpha(t)$ is defined by Eq. (14). The part of the equations associated with the isolated motion of the particle and also with the interaction between the particle and the bath is the same as in Zwanzig's model. It can be derived from a time-independent Hamiltonian. It is only the dynamics of the bath particles what has been modified by introducing a term that is going to be responsible for the change of the temperature in the bath.

3. GENERALIZED LANGEVIN EQUATION

To derive a generalized Langevin equation, we follow Zwanzig's procedure.⁽²⁾ The formal solutions of Eqs. (15) and (16) can be written as

$$R(t) q_j(t) = \frac{\gamma_j}{\omega_j^2} R(t) Q(t) + \left[q_j(0) - \frac{\gamma_j}{\omega_j^2} Q(0) \right] \cos \omega_j t + \frac{p_j(0)}{\omega_j} \sin \omega_j t - \frac{\gamma_j}{\omega_j^2} \int_0^t d\tau \cos[\omega_j(t - \tau)] \frac{d}{d\tau} (R(\tau) Q(\tau)) \tag{17}$$

and

$$R(t) p_j(t) = -\omega_j \left[q_j(0) - \frac{\gamma_j}{\omega_j^2} Q(0) \right] \sin \omega_j t + p_j(0) \cos \omega_j t + \frac{\gamma_j}{\omega_j} \int_0^t d\tau \sin(\omega_j(t - \tau)) \frac{d}{d\tau} (R(\tau) Q(\tau)) \tag{18}$$

with

$$R(t) = \left(\frac{T(0)}{T(t)} \right)^{1/2} \tag{19}$$

When these expressions are introduced into Eqs. (4) and (5), the desired generalized Langevin equation is obtained:

$$M \frac{dQ(t)}{dt} = P(t) \tag{20}$$

$$\begin{aligned} \frac{dP(t)}{dt} = & -U'(Q(t)) - \int_0^t dt' \zeta(t-t') \left(\frac{T(t)}{T(t')} \right)^{1/2} \\ & \times \left[\frac{P(t')}{M} - \frac{1}{2} Q(t') \frac{d}{dt'} \ln T(t') \right] + F(t) \end{aligned} \tag{21}$$

where $F(t)$ depends on the initial conditions and also on the function $T(t)$,

$$F(t) = R(t)^{-1} \sum_j \gamma_j \left[q_j(0) - \frac{\gamma_j}{\omega_j^2} Q(0) \right] \cos \omega_j t \\ + R(t)^{-1} \sum_j \gamma_j \frac{p_j(0)}{\omega_j} \sin \omega_j t \quad (22)$$

and the friction coefficient $\zeta(t)$ is given by

$$\zeta(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos \omega_j t \quad (23)$$

Now an initial ensemble of states is introduced in order to specify the statistical properties of the bath-dependent term, $F(t)$. We assume that for given values of $Q(0)$ and $P(0)$ the bath was at equilibrium in the presence of the particle. In other words, we consider a probability distribution of the form

$$W(Q(0), P(0), \{q_j(0)\}, \{p_j(0)\}) \propto \varphi(Q(0), P(0)) \exp -\frac{H_b}{k_B T(0)} \quad (24)$$

φ is an arbitrary function. In this ensemble

$$\langle F(t) \rangle = 0 \quad (25)$$

and

$$\langle F(t) F(t') \rangle = k_B [T(t) T(t')]^{1/2} \zeta(t-t') \quad (26)$$

Equation (26) is a fluctuation-dissipation theorem for our model, relating the fluctuating force and the transport coefficient. From Eqs. (22) and (24) it follows that $F(t)$ defines a Gaussian process, and therefore Eqs. (25) and (26) completely determine its statistical properties.

Of course, if the temperature is taken to be constant, one recovers Zwanzig's results in ref. 2. The effect of a time-dependent temperature shows up in several ways. First, the two-time correlation function of the fluctuating force contains the square root of the product of the temperatures at both times, Eq. (26). Second, the friction term also has a time-dependent temperature factor. Finally, the most significant modification is the appearance of a new term in the generalized Langevin equation. This term has the same structure as the usual friction term, but the position of the particle appears instead of its momentum. In addition, it is related to the change of the logarithm of the temperature along the evolution of

the particle. On the other hand, the friction coefficient $\zeta(t)$ is not affected by the change of the temperature.

Next, let us see what happens in the Markovian approximation. We consider a distribution of frequencies of the bath particles of the Debye type. We also take $\gamma_i = N^{-1/2}\gamma$ for all i . Then, for values of the cutoff frequency ω_d big enough, one finds

$$\zeta(t) = 2\zeta_0 \delta(t) \quad (27)$$

where

$$\zeta_0 = \frac{3\pi\gamma^2}{2\omega_d^3} \quad (28)$$

When Eq. (27) is introduced into Eq. (21), the result is the Markovian equation

$$\frac{dP(t)}{dt} = -U'(Q(t)) - \zeta_0 \left(\frac{P(t)}{M} - \frac{1}{2} Q(t) \frac{d}{dt} \ln T(t) \right) + F(t) \quad (29)$$

with the Gaussian force $F(t)$ satisfying

$$\begin{aligned} \langle F(t) \rangle &= 0 \\ \langle F(t) F(t') \rangle &= 2k_B T(t) \zeta_0 \delta(t-t') \end{aligned} \quad (30)$$

Equation (30) has the form that one could expect for the fluctuation-dissipation theorem in the Markovian limit, once the theorem is known for the constant-temperature case. Nevertheless, the presence of the term proportional to $Q(t)$ in Eq. (29) seems difficult to guess from the equation at constant temperature.

Since the fluctuations in Eq. (29) are Gaussian and delta-correlated, the conditional probability $W(Q, P, t | Q', P', t')$ for the particle position and momentum can be easily shown to obey the Fokker-Planck equation

$$\begin{aligned} \frac{\partial}{\partial t} W(Q, P, t | Q', P', t') &= \left[-\frac{P}{M} \frac{\partial}{\partial Q} + \left(U'(Q) - \frac{1}{2} \zeta_0 Q \frac{d}{dt} \ln T \right) \frac{\partial}{\partial P} \right. \\ &\quad \left. + \zeta_0 \frac{\partial}{\partial P} \frac{P}{M} + k_B T(t) \zeta_0 \frac{\partial^2}{\partial P^2} \right] W(Q, P, t | Q', P', t') \end{aligned} \quad (31)$$

It is easily verified that in the limit $N \rightarrow \infty$ the bath is well described by a distribution function of the equilibrium type with a time-dependent

temperature $T(t)$. This is due to the fact that the effect of the particle on the distribution function of the bath becomes negligible. Therefore, $T(t)$ can be interpreted as the actual temperature of the bath.

One needs to be careful if this model is used to describe heating processes. The deterministic equations, neglecting fluctuations, associated with Eqs. (20) and (29) are

$$M \frac{dQ}{dt} = P \quad (32)$$

and

$$\frac{dP}{dt} = -U'(Q) - \zeta_0 \left(\frac{P}{M} - \frac{1}{2} Q \frac{d}{dt} \ln T \right) \quad (33)$$

If $T(t) > 0$, Eqs. (32) and (33) can lead to runaway solutions, as is the case, for instance, when $U'(Q) = 0$. Of course, this is a very specific feature of our system, and it is not to be expected to hold in more realistic models.

4. FINAL REMARKS

The main result of this paper is Eq. (21), describing the time evolution of the momentum of a particle in contact with a bath whose temperature changes in time. An important point is to what extent the form of Eq. (21) depends on the specific form we have assumed for the dynamical equations of the bath particles in order to control the temperature. From the derivation in the main text and also from the Appendix it seems clear that the results are very much influenced by this choice. But, at the same time, it seems also true that in all cases new terms appear in the Langevin equation as compared with the constant-temperature case.

Also, the effect on the particle due to heating or cooling the bath strongly depends on the kind of coupling between both of them. Therefore, the conclusions with our model cannot be trivially extended to more realistic or complicated systems. In any case, we think that this model may be useful for pointing out the difficulties that can appear if one tries to extend mesoscopic equations to describe the evolution of a system with a time-dependent temperature.

APPENDIX

In this Appendix we show that the temperature of the bath can also be controlled by means of the introduction of a time-dependent term in the Hamiltonian given by Eq. (1). If we denote this term by

$$\sum A(q_j, p_j, t) \quad (A.1)$$

the dynamical equations for the position and momentum of the j th particle of the bath (in absence of the system particle) are

$$\frac{d}{dt} q_j = p_j + \frac{\partial}{\partial p_j} A(q_j, p_j, t) \quad (\text{A.2})$$

$$\frac{d}{dt} p_j = -\omega_j^2 q_j - \frac{\partial}{\partial q_j} A(q_j, p_j, t) \quad (\text{A.3})$$

The corresponding evolution equation for the distribution function is

$$\begin{aligned} \frac{\partial}{\partial t} f(q_j, p_j, t) = & - \left(p_j + \frac{\partial A}{\partial p_j} \right) \frac{\partial}{\partial q_j} f(q_j, p_j, t) \\ & + \left(\omega_j^2 q_j + \frac{\partial A}{\partial q_j} \right) \frac{\partial}{\partial p_j} f(q_j, p_j, t) \end{aligned} \quad (\text{A.4})$$

When the distribution function given by Eq. (12) is required to be a solution of Eq. (A.4), one gets the following first-order partial differential equation:

$$p_j \frac{\partial A}{\partial q_j} - \omega_j^2 q_j \frac{\partial A}{\partial p_j} + \frac{1}{2} [p_j^2 + \omega_j^2 q_j^2 - 2k_B T(t)] \frac{d}{dt} \ln T(t) = 0 \quad (\text{A.5})$$

This equation is linear and it can be solved by the characteristics method. The general solution is

$$\begin{aligned} A(q_j, p_j, t) = & \frac{1}{\omega_j} \left[\frac{d}{dt} \ln T(t) \right] \left[k_B T(t) - \frac{p_j^2}{2} - \frac{1}{2} \omega_j^2 q_j^2 \right] \\ & \times \arcsin \frac{q_j \omega_j}{(p_j^2 + \omega_j^2 q_j^2)^{1/2}} + \Phi \left(\frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 q_j^2 \right) \end{aligned} \quad (\text{A.6})$$

where Φ is an arbitrary function. In this way, we have the general expression of a Hamiltonian that is able to control the temperature of the bath, keeping it at equilibrium. Nevertheless, the equations of motion for the heat bath particles in presence of the system particle seem hard to solve, even with the simplest possible choice for Φ .

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