

# A Statistical Mechanical Approximation for the Calculation of Time Auto-Correlation Functions

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This paper<sup>1</sup> considers the problem of estimating the time auto-correlation function for a quantity that is defined in configuration space, given a knowledge of the mean-square displacement as function of time in configuration space. The problem is particularly relevant for viscous liquids, where the interesting time-scales are often beyond those reachable by computer simulation. An approximate formula is derived which reduces the calculation of the time auto-correlation function to a "double canonical" average. In this approximation, in the case of Langevin dynamics the mean-square displacement itself may be evaluated from the "double partition function". The scheme developed is illustrated by computer simulations of a simple one-dimensional system at different temperatures, showing good agreement between the exact time auto-correlation functions and those found by the approximation.

The calculation of a time auto-correlation function<sup>2-4</sup> is a straightforward matter in any computer simulation tracing the time evolution of a system<sup>5-7</sup>. However, computer simulations are not feasible today on time scales longer than microseconds. These time scales are relevant, e.g., for viscous liquids approaching the glass transition. Therefore, one cannot by simulation calculate a number of experimentally easily accessible quantities in highly viscous liquids like the frequency-dependent viscosity<sup>8</sup>, bulk modulus<sup>9</sup>, dielectric constant<sup>10</sup>, or specific heat<sup>11,12</sup> (quantities that all via the fluctuation-dissipation theorem<sup>2-4</sup> are given as Laplace transforms of an equilibrium time auto-correlation function. In this situation one would like to have an approximate theory at hand. Focussing only on time auto-correlation functions of quantities  $A(X)$  that are defined in configuration space,  $X = (X_1, \dots, X_n)$ , an approximation is proposed below, based on an ansatz for the joint probability of initial point  $X$  at  $t = 0$  and final point  $X'$  after time  $t$ , denoted by  $P(X, X'; t)$ . This joint probability directly determines the time auto-correlation function via

$$\langle A(0)A(t) \rangle = \int dX dX' A(X)A(X')P(X, X'; t). \quad (1)$$

If  $Z$  is the configurational partition function, given in terms of  $\beta = 1/(k_B T)$  and the potential energy  $U(X)$  as

$$Z(\beta) = \int dX e^{-\beta U(X)}, \quad (2)$$

and  $G(X \rightarrow X'; t)$  is the Green's function, the exact expression for the joint probability is

$$P(X, X'; t) = \frac{e^{-\beta U(X)}}{Z} G(X \rightarrow X'; t). \quad (3)$$

However, Eq. (3) is not very useful unless the Green's function is known. Note that the principle of detailed balance - expressing the time-reversal invariance of the equations of motion - implies that  $P(X, X'; t) = P(X', X; t)$ , a requirement that any approximation should also satisfy.

The exact method for calculating the time auto-correlation function  $\langle A(0)A(t) \rangle$  is illustrated in Fig. 1 showing the path in configurational space. At a number of times  $t_1, \dots, t_p$  one computes the product  $A(X(t_j))A(X(t_j + t))$ , and  $\langle A(0)A(t) \rangle$  is the average of this quantity as  $p \rightarrow \infty$ . Assuming here and henceforth that the  $X_i$ 's are simple rectangular coordinates and that  $\langle A \rangle = 0$ , one always expects  $\langle A(0)A(t) \rangle \rightarrow 0$  as  $t \rightarrow \infty$ . This loss of correlation after long time comes about because the point in configuration space at time  $t$ ,  $X'$ , for large  $t$  is far away from the initial point  $X$ . A measure of the distance travelled in time  $t$  is provided by the mean-square displacement,  $\langle \Delta X^2(t) \rangle$ . This quantity, of course, is defined by

$$\langle \Delta X^2(t) \rangle = \langle (X - X')^2 \rangle \equiv \sum_{i=1}^n \langle (X_i - X'_i)^2 \rangle. \quad (4)$$

Assuming that the mean-square displacement itself is a known function of time, the idea is now to estimate  $\langle A(0)A(t) \rangle$  via the "spatial" auto-correlation of  $A$  in configuration space evaluated at a distance equal to  $\sqrt{\langle \Delta X^2(t) \rangle}$ .

Before proceeding, we briefly discuss the physics of this way of thinking about the time auto-correlation function. A simple case is when the mean-square displacement is proportional to time (for large times this is, of course, always the case). In this case, if the "spatial" correlation of  $A$  has a Gaussian distance decay, the time auto-correlation function is a simple exponential, corresponding to Debye relaxation. If, however, the spatial correlation of  $A$  has an exponential decay, the time auto-correlation function is a stretched exponential with exponent 1/2. The latter case gives a reasonable fit to many experiments on viscous liquids<sup>13</sup>. The above picture of decomposing the time-autocorrelation function into A) a "geometric" correlation and B) the distance travelled in a given time, is in harmony with another well-known property of viscous liquids. In these systems all linear relaxation functions determine roughly the same average relaxation time, a time which increases dramatically upon cooling. In the above "geometric" picture this is simply a consequence of the motion slowing down in configuration space, whereas "spatial" correlations in many cases probably only change little upon cooling.

We now turn to the problem of estimating the joint probability  $P(X, X'; t)$ . In the thermodynamic limit ( $n \rightarrow \infty$ ) the relative fluctuations in the mean-square displacement go to zero, and therefore the distance between  $X = X(t_j)$  and  $X' = X(t_j + t)$  is "precisely" equal to  $\sqrt{\langle \Delta X^2(t) \rangle}$ . Similarly, the relative fluctuations in potential energy go to zero, so the potential energy of both points  $X$  and  $X'$  is "equal to"  $\langle U \rangle = -\frac{\partial \ln Z}{\partial \beta}$ . Now, the basic idea is an ansatz for  $P(X, X'; t)$  that assumes equal probability for all pairs of points with correct distance and correct potential energy. Thus,

$$P(X, X'; t) \propto \delta[(X - X')^2 - \langle \Delta X^2(t) \rangle] \delta[U(X) - \langle U \rangle] \delta[U(X') - \langle U \rangle]. \quad (5)$$

In the thermodynamic limit there is "equipartition" between  $U(X)$  and  $U(X')$ , and the last two delta functions may be replaced by a single delta function, leading to

$$P(X, X'; t) \propto \delta[(X - X')^2 - \langle \Delta X^2(t) \rangle] \delta[U(X) + U(X') - 2\langle U \rangle]. \quad (6)$$

The next step is to convert Eq. (6) to a "canonical" form, which is computationally much more convenient than the present "microcanonical" form. This is done by replacing the first delta function by  $\exp[-a(X - X')^2]$  where  $a$  is a Lagrangian multiplier adjusted to give the correct mean-square displacement. Similarly, the second delta function is replaced by  $\exp[-b[U(X) + U(X')]]$  where  $b$  is adjusted to ensure that the average of  $U(X) + U(X')$  is  $2\langle U \rangle$ . If the following "double partition function"

$$D(a, b) = \int dX dX' e^{-a(X - X')^2 - b[U(X) + U(X')]} \quad (7)$$

is introduced, the final expression for approximately calculating the time auto-correlation function is

$$\langle A(0)A(t) \rangle = \frac{\int dX dX' A(X)A(X') e^{-a(X - X')^2 - b[U(X) + U(X')]} D(a, b)}{D(a, b)}. \quad (8)$$

In the thermodynamic limit Eq. (8) is equivalent to calculating the average of Eq. (1) by using Eq. (5).

The two parameters  $a$  and  $b$  are determined in the following way. First,  $b = b(a)$  is found from the condition that the average joint potential energy of initial and final point is  $2\langle U \rangle$ . Thus,  $b = b(a)$  is determined from the condition that this average is independent of  $a$ :

$$\frac{d}{da} \frac{\partial \ln D}{\partial b} = 0. \quad (9)$$

Since  $\frac{d}{da} = \partial_a + \frac{db}{da} \partial_b$  [with standard abbreviation for partial derivatives], the expansion of Eq. (9) leads to the following first order differential equation for  $b = b(a)$ :

$$\frac{db}{da} = \frac{\partial_a D \partial_b D - D \partial_{ab} D}{D \partial_b^2 D - (\partial_b D)^2}. \quad (10)$$

Once the function  $b(a)$  has been determined,  $a = a(t)$  is found from requiring that the mean-square displacement calculated from  $D(a, b(a))$  is correct:

$$-\frac{\partial \ln D}{\partial a} = \langle \Delta X^2(t) \rangle. \quad (11)$$

The short and long time limits are determined as follows. For  $a(t)$  one clearly has

$$a(t=0) = \infty \text{ and } a(\infty) = 0. \quad (12)$$

In the limit of large times  $X$  and  $X'$  are far apart and  $U(X)$  is uncorrelated with  $U(X')$ . In this limit  $b = \beta$ :

$$b(a=0) = \beta. \quad (13)$$

In the short time limit the points  $X$  and  $X'$  are close. Thus,  $P(X, X'; t) \propto \delta[X - X'] \exp[-2bU(X)]$  for  $t \rightarrow 0$  and Eq. (1) yields

$$\lim_{t \rightarrow 0} \langle A(0)A(t) \rangle = \frac{\int dX A^2(X) e^{-2bU(X)}}{\int dX e^{-2bU(X)}}. \quad (14)$$

For this to give the correct canonical average one must have  $b = \beta/2$ , i.e.,

$$b(a = \infty) = \frac{\beta}{2}. \quad (15)$$

As we will show now, the short time behavior of  $a(t)$  may be derived directly from the equations of motion. In the case of Newtonian dynamics, the Green's function at short times is easily found from the integrated equations of motion, where the momentum is distributed according to a Gaussian (for simplicity all particles are assumed to have equal mass,  $m$ )

$$G(X \rightarrow X'; t) \propto \exp \left[ -\frac{\beta}{2m} \sum_{i=1}^n \left( \frac{m}{t} (X'_i - X_i) + \frac{1}{2} \partial_i U t \right)^2 \right]. \quad (16)$$

To first order in  $t$  this becomes

$$G(X \rightarrow X'; t) \propto \exp \left[ -a(t)(X - X')^2 - \frac{\beta}{2} [U(X') - U(X)] \right], \quad (17)$$

where

$$a(t) = \frac{\beta m}{2t^2} \text{ [Newtonian dynamics, } t \rightarrow 0]. \quad (18)$$

Note that via Eq. (3) this Green's function confirms the form of Eq. (8) for  $t \rightarrow 0$ , as well as the boundary condition Eq. (15). Next, we consider the case of Langevin dynamics,

$$\dot{X}_i = -\mu \frac{\partial U}{\partial X_i} + \xi_i(t), \quad (19)$$

with the standard Gaussian white noise term<sup>15</sup>  $\langle \xi_i(t) \xi_j(t') \rangle = 2\mu k_B T \delta_{i,j} \delta(t - t')$ . From the equations of motion one finds that, because the integrated noise term is Gaussianly distributed,

$$G(X \rightarrow X'; t) \propto \exp \left[ -\frac{\beta}{4\mu t} \sum_{i=1}^n (X'_i - X_i + \mu \partial_i U t)^2 \right]. \quad (20)$$

At short times this again leads to Eq. (17), where however now

$$a(t) = \frac{\beta}{4\mu t}, \text{ [Langevin dynamics, } t \rightarrow 0]. \quad (21)$$

In the case of Langevin dynamics Eq. (8) may be applied to the calculation of the force-force time auto-correlation function. This leads to an equation that in principle allows a calculation of  $\langle \Delta X^2(t) \rangle$  directly from the double partition function: The mean-square displacement in time  $t$  is given by (sum over repeated indices)

$$\langle \Delta X^2(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle \dot{X}_i(t') \dot{X}_i(t'') \rangle. \quad (22)$$

Since the noise terms are uncorrelated at different times, Eqs. (19) and (22) imply

$$\frac{d^2}{dt^2} \langle \Delta X^2(t) \rangle = 2 \langle \dot{X}_i(0) \dot{X}_i(t) \rangle = 2\mu^2 \langle \partial_i U(0) \partial_i U(t) \rangle. \quad (23)$$

From Eq. (8) the force-force time auto-correlation function is rewritten as

$$\langle \partial_i U(0) \partial_i U(t) \rangle = \frac{1}{b^2} \int \frac{dX dX'}{D(a, b)} \left[ \partial_i e^{-bU(X)} \right] \left[ \partial'_i e^{-bU(X')} \right] e^{-a(X-X')^2}. \quad (24)$$

By partial integrations one finds

$$\langle \partial_i U(0) \partial_i U(t) \rangle = -4 \frac{a^2}{b^2} \int \frac{dX dX'}{D(a, b)} (X - X')^2 e^{-a(X-X')^2 - b[U(X) + U(X')]} = 4 \frac{a^2}{b^2} \frac{\partial \ln D}{\partial a}. \quad (25)$$

Thus, the equation for  $a(t)$  is from Eqs. (11), (23) and (25)

$$\left( \frac{d^2}{dt^2} + 8\mu^2 \frac{a^2}{b^2} \right) \frac{\partial \ln D}{\partial a} = 0. \quad (26)$$

The expansion of Eq. (26) is straightforward, though tedious.

In order to check the validity of Eq. (8) a simple system obeying Langevin dynamics was studied numerically. The system was chosen to be so simple that the integral of Eq. (8) may be evaluated "exactly", thus avoiding the noise of Monte Carlo simulations. No attempts were made to verify that Eq. (26) gives the correct  $a(t)$ . Instead, the following procedure was followed. At a number of fixed  $a$ -values  $b(a)$  was found from the requirement that the average joint potential energy is  $2\langle U \rangle$ . Then the mean-square displacement was evaluated for each  $a$  from Eq. (11) and also as function of time from the dynamical simulations, allowing an identification of the times corresponding to the fixed  $a$ -values. Finally, the time auto-correlation function was calculated from Eq. (8) at the fixed  $a$ -values. Figure 2 shows the results for the following time auto-correlation function  $\langle X^3(0)X^3(t) \rangle$  for a particle in a double well potential obeying Langevin dynamics<sup>14</sup>. The full curve is the exact time auto-correlation function found by solving the Smoluchowski equation<sup>15</sup> and the dots give the prediction of Eq. (8). Results are shown for the cases  $\beta = 2$  and  $\beta = 8$  in dimensionless units. There is good agreement between prediction and simulation.

To conclude, in this paper a statistical mechanical approximation for the calculation of time auto-correlation functions has been proposed. The formalism assumes a knowledge of the mean-square displacement in configuration space as a function of time, the mean-square displacement acting as a "molecular clock". The remaining "spatial" auto-correlation is a "double" canonical average (Eq. (8)). Note that the "double partition function",  $D(a, b)$ , contains the ordinary partition function (of configuration space) as a special case:  $Z^2(\beta) = D(0, \beta)$ .

The approximation proposed is only useful if  $\langle \Delta X^2(t) \rangle$  is known. Experimentally, this quantity is accessible via the intermediate incoherent scattering function. In some cases phenomenological estimates of the mean-square displacement as function of time may be given. Thus, for hopping in a rugged energy landscape where all minima are equal, the mean-square displacement is **universal** at low temperatures (except for trivial scalings), i.e., independent of the barrier height probability distribution. This has been shown<sup>16</sup> by the effective medium approximation and by computer simulations of the frequency-dependent conductivity (which is simply related to the mean-square displacement<sup>17</sup>). Finally, there is the possibility that the mean-square displacement may be found approximately from Eq. (26) if Langevin dynamics is assumed, as is common, e.g., in polymer dynamics<sup>18</sup>.

Equation (26) signals that Langevin dynamics plays a special role in the proposed scheme for calculation of time auto-correlation functions. A question of considerably interest is if and when Langevin dynamics can be expected to give the same time auto-correlation functions as Newtonian dynamics<sup>19</sup>. If the ansatz proposed above is correct, two different dynamics give the same time auto-correlation functions for any quantity defined in configuration space, if the two dynamics just give the same mean-square displacement as function of time. In this way the ansatz provides a mechanism for the consistency of any two types of dynamics.

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- <sup>1</sup> The paper was submitted to Phys. Rev. B in the spring of 1994, but not accepted without revision. I have not yet taken the time to correct the paper according to the reviewers suggestions. One point made in the referee report should be mentioned here: The reviewer pointed out that Haan in 1979 proposed a related idea [S. W. Haan, Phys. Rev. A 20, 2516 (1979)]. Haan worked in real 3d-space and not in configuration space, but his work (of which I was unaware) is clearly built on the same thinking as presented here. The reviewer is thanked for pointing this out.
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FIG. 1. .

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