

Efficient Measurement of Linear Susceptibilities in Molecular Simulations: Application to Aging Supercooled Liquids

Ludovic Berthier

Laboratoire des Colloïdes, Verres et Nanomatériaux, UMR 5587, Université Montpellier II and CNRS, 34095 Montpellier, France

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We propose a novel method to measure time-dependent linear susceptibilities in molecular simulations, which does not require the use of nonequilibrium simulations, subtraction techniques, or fluctuation-dissipation theorems. The main idea is an exact reformulation of linearly perturbed quantities in terms of observables accessible in a single unperturbed trajectory. We apply these ideas to supercooled liquids in a nonequilibrium aging regime. We show that previous work had underestimated deviations from fluctuation-dissipation relations in the case of a Lennard-Jones system, while our results for silica are in qualitative disagreement with earlier results.

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Correlation and response functions play a major role in condensed matter physics as they directly probe static and dynamic properties at a microscopic level [1]. At thermal equilibrium, linear response theory permits the derivation of fluctuation-dissipation relations between conjugated susceptibilities and correlations, so that both types of measurements become equivalent [2]. Numerical simulations mainly focus on spontaneous fluctuations and probe microscopic dynamics via correlation functions [3]. However, there exist cases where the numerical measurement of response functions becomes necessary, for instance when correlation functions become too noisy to be detected [4], or in nonequilibrium situations, where correlation and response functions contain distinct information because fluctuation-dissipation theorems (FDT) do not hold [5]. Quantifying FDT “violations” from the simultaneous measurement of correlation and response functions is an increasingly active field of research for both experiments and theory, which spreads from glassy materials to a larger variety of complex systems; see [6] for a review. Here we propose an efficient method to access linear response functions in numerical simulations of molecular systems and apply it to study response functions of glass-forming liquids. It allows us to quantify in an unbiased way FDT violations in aging liquids and to resolve the “paradoxical” behavior reported in Ref. [7] for aging silica, the most widely used glass former.

Direct measurements of linear susceptibilities usually proceed as follows. Consider a system of N particles described by coordinates, $\vec{r} \equiv \{\vec{r}_i, i = 1, \dots, N\}$, momenta, $\vec{p} \equiv \{\vec{p}_i, i = 1, \dots, N\}$, masses m_i , and a Hamiltonian $\mathcal{H}(\vec{r}, \vec{p})$ containing a kinetic part, $\mathcal{K}(\vec{p}) = \sum_i \vec{p}_i^2 / (2m_i)$, and a potential part, $\mathcal{V}(\vec{r})$. We first consider Newtonian dynamics, as used in molecular dynamics (MD):

$$\dot{\vec{r}}_i = \partial \mathcal{H} / \partial \vec{p}_i, \quad \dot{\vec{p}}_i = -\partial \mathcal{H} / \partial \vec{r}_i. \quad (1)$$

Observables, $A(t) \equiv A[\vec{p}(t), \vec{r}(t)]$, can be measured at any time in a simulation, and correlation functions, $C(t, t') =$

$\langle A(t)B(t') \rangle_0$, are obtained by averaging over repeated measurements. The subscript “0” indicates averages performed over unperturbed trajectories, and we suppose $\langle A(t) \rangle_0 = 0$. In time-translationally invariant systems, two-time quantities only depend on $t - t'$ but we retain the (t, t') notation adapted to aging systems.

To measure response functions, an external field of constant amplitude h , conjugated to $B(t)$, is introduced at time t' , such that the Hamiltonian contains the additional term $\delta \mathcal{H} = -hB$ for $t > t'$. A linear susceptibility can then be defined:

$$\chi(t, t') = \int_{t'}^t dt'' \frac{\partial \langle A(t) \rangle_h}{\partial h(t'')} \Big|_{h \rightarrow 0}. \quad (2)$$

Step responses are considered for simplicity but the discussion holds more generally. The average in (2) is with the field switched on, the zero-field limit comes from repeated measurements with fields of decreasing amplitude. In practice, a compromise is sought between large fields introducing unwanted nonlinear effects, and small fields resulting in poor signals. Such nonequilibrium techniques suffer from a serious drawback. Averages in (2) are taken over perturbed trajectories, so that susceptibilities can only be measured one at a time, contrary to correlation functions which can be simultaneously measured and time averaged in a single unperturbed trajectory.

An alternative would be to perform the derivative in Eq. (2) *before* taking the average. This is precisely how the FDT is derived [2]. Averages are first expressed in terms of the distribution function. Its thermal equilibrium (Gibbs-Boltzmann) form at temperature T is then assumed, and the derivative is computed analytically [2]:

$$\chi(t, t') = \frac{1}{T} [C(t, t) - C(t, t')], \quad (3)$$

where we have set Boltzmann’s constant to unity. An important and well-known feature of the FDT in Eq. (3) is that the right-hand side is evaluated using unperturbed trajectories, the temperature prefactor reminding us that

thermal equilibrium is assumed, implying that Eq. (3) cannot be used to measure $\chi(t, t')$ far from equilibrium.

Here, we shall perform the derivative before doing the average *without* assuming thermal equilibrium. In MD simulations, the subtraction technique [8] is a finite-field approximation of this idea: two simulations start from the same configuration at time t' , one with $h = 0$, the other with a small field, h . The susceptibility reads: $\chi(t, t') \approx (\langle A(t) \rangle - \langle A(t) \rangle_0)/h$. Nonequilibrium techniques are in fact unnecessary [8], since the $h \rightarrow 0$ limit can be taken directly from (1) using perturbation theory [9] to devise an unperturbed technique. The quantities $\tilde{\chi}_i \equiv \partial \tilde{r}_i / \partial h$ and $\tilde{\varphi}_i \equiv \partial \tilde{p}_i / \partial h$ evolve as [9]:

$$\begin{aligned} \dot{\tilde{\chi}}_i &= \frac{\tilde{\varphi}_i}{m_i} - \frac{\partial B(\vec{r}, \vec{p})}{\partial \tilde{p}_i}, \\ \dot{\tilde{\varphi}}_i &= \frac{\partial B(\vec{r}, \vec{p})}{\partial \tilde{r}_i} - \sum_{j=1}^N \frac{\partial^2 \mathcal{V}(\vec{r})}{\partial \tilde{r}_i \partial \tilde{r}_j} \cdot \tilde{\chi}_j. \end{aligned} \quad (4)$$

The susceptibility $\chi(t, t')$ can now be evaluated from *unperturbed* trajectories:

$$\chi(t, t') = \left\langle \sum_{i=1}^N \left(\frac{\partial A(\vec{r}, \vec{p})}{\partial \tilde{r}_i} \cdot \tilde{\chi}_i + \frac{\partial A(\vec{r}, \vec{p})}{\partial \tilde{p}_i} \cdot \tilde{\varphi}_i \right) \right\rangle_0. \quad (5)$$

To illustrate the result in Eq. (5) we have performed MD simulations of a 80:20 binary Lennard-Jones (LJ) system composed of $N = 10^3$ particles at density $\rho = 1.2$. Particles interact with a LJ potential with parameters that can be found in [10], chosen to avoid crystallization at low temperature, and to study the properties of glass-forming liquids. Technical details of our simulations are as in the original paper [10]. When the temperature gets lower than $T \approx 1$ (we use LJ units [10]), the dynamics dramatically slows down, and the system cannot be equilibrated in computer simulations below $T \approx 0.43$.

We perform equilibrium simulations where we simultaneously solve (1) and (4) to evaluate $\chi(t, t')$ from (5), and the correlation $C(t, t')$. We focus on the following observables: $A(t) = N^{-1} \sum_j \epsilon_j \exp[i\vec{k} \cdot \vec{r}_j(t)]$ and $B(t) = 2 \sum_j \epsilon_j \cos[\vec{k} \cdot \vec{r}_j(t)]$, where $\epsilon_j = \pm 1$ is a bimodal random variable of mean 0 [2], such that $C(t, t')$ corresponds to the self-intermediate scattering function [2]. For $T = 1.0$, dynamics is fast and $\chi(t, t')$ can be evaluated in a few runs, as can be checked using the FDT. For $T = 0.75$, where the relaxation time is ≈ 50 (see inset of Fig. 1), a fundamental limitation appears. In Fig. 1 we represent $T\chi(t, t')$ evaluated from 10^3 independent runs using (5), as a function of $C(t, t')$. FDT predicts the linear relation shown as a full line. For $t - t' \lesssim 5$, $\chi(t, t')$ follows the FDT. For larger $t - t'$, the noise in the susceptibility diverges exponentially (due to the chaotic nature of trajectories) and no reliable measurement can be performed, just as in subtraction techniques. No-field methods are therefore of little use in MD simulations of supercooled liquids where large times are needed.

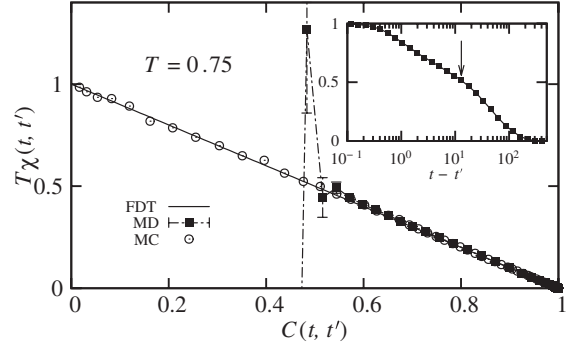


FIG. 1. Simultaneous measurement of susceptibility $\chi(t, t')$ and correlation $C(t, t')$ in 10^3 independent unperturbed trajectories at $T = 0.75$ in the LJ system using Eq. (5) for MD and Eq. (7) for MC simulations. For MD the noise diverges exponentially and $\chi(t, t')$ cannot be evaluated for $t - t' > 10$, as indicated in the inset showing $C(t, t')$ measured in MD. In MC simulations $\chi(t, t')$ perfectly follows the FDT prediction indicated by a full line over the whole time range.

The above exercise suggests that in Monte Carlo (MC) simulations, where phase space is sampled probabilistically rather than deterministically, response functions could be efficiently evaluated. Similar ideas were recently discussed for discrete spins [11]. In a standard MC simulation [3], a configuration C_t is reached at time t . A trial configuration C'_t is accessed with acceptance rate $A_{C_t \rightarrow C'_t}$, generally defined from the energy change between the two configurations. Here we use the standard strategy of local and sequential moves of individual particles, which are accepted according to the Metropolis acceptance rate [3]. The transition probability from C_t to C_{t+1} reads: $\mathcal{W}_{C_t \rightarrow C_{t+1}} = \delta_{C_{t+1}, C'_t} A_{C_t \rightarrow C'_t} + \delta_{C_{t+1}, C_t} (1 - A_{C_t \rightarrow C'_t})$. Averages now mean sampling a large number \mathcal{N} of trajectories, $\langle A(t)B(t') \rangle_0 = \mathcal{N}^{-1} \sum_{k=1}^{\mathcal{N}} A_k(t)B_k(t')P_k(t' \rightarrow t)$, where $A_k(t)$ is the value of A at time t in trajectory k , and $P_k(t' \rightarrow t)$ is the probability of trajectory k between times t' and t starting from $C_{t'}$, $P_k(t' \rightarrow t) = \prod_{t''=t'}^{t-1} \mathcal{W}_{C_{t''} \rightarrow C_{t''+1}}^k$, where $C_{t''}^k$ is the configuration visited at time t'' in trajectory k . The susceptibility reads $\chi(t, t') = \partial_h \langle A(t) \rangle = \partial_h [\mathcal{N}^{-1} \sum_k A_k(t)P_k(t' \rightarrow t)]$. Applying an infinitesimal field simply modifies the acceptance rates, and therefore the transition probabilities $\mathcal{W}_{C_t \rightarrow C_{t+1}}$, so that the derivative ∂_h only acts on $P_k(t' \rightarrow t)$. We find

$$\partial_h P_k(t' \rightarrow t) = P_k(t' \rightarrow t) \sum_{t''=t'}^{t-1} \frac{\partial_h (\mathcal{W}_{C_{t''} \rightarrow C_{t''+1}})}{\mathcal{W}_{C_{t''} \rightarrow C_{t''+1}}}, \quad (6)$$

and $\chi(t, t')$ can be rewritten as an *unperturbed* average,

$$\chi(t, t') = \langle A(t)R(t' \rightarrow t) \rangle_0, \quad (7)$$

where $R(t' \rightarrow t) \equiv \sum_{t''} \partial_h \ln(\mathcal{W}_{C_{t''} \rightarrow C_{t''+1}}^k)$. In Fig. 1 we report the simultaneous measurement of $\chi(t, t')$, estimated via (7), and of $C(t, t')$ using 10^3 independent MC runs of the binary Lennard-Jones mixture described above for $T = 0.75$. (The details of the numerics appeared recently

[12].) The measurement now easily extends to the whole range of time scale over which $C(t, t')$ changes, and FDT is perfectly obeyed. Although MC trajectories are chaotic, no exponential divergence of the noise is observed, at variance with the MD case. What Eq. (7) in fact does is to use a *single* unperturbed trajectory to evaluate the value the observable $A(t)$ would have taken if an infinitesimal field had been applied. Additionally, the evaluation of Eq. (7) is computationally free since it only requires updating one additional observable, $R(t' \rightarrow t)$, during the production of unperturbed trajectories. Finally, several susceptibilities and correlations may now be computed during the same simulation, and time averaging is easily implemented. The main limitation of the method is again statistics: $\chi(t, t')$ now takes the form of a multitime correlator, and its measurement becomes statistically costly as $t - t'$ gets too large. We find an algebraic growth of the noise, as in spin systems [11], which is nevertheless a drastic improvement over exponential growth. This will allow us to study aging systems below. A second drawback is the need to replace Newtonian by Monte Carlo dynamics since the resulting *dynamics* are not necessarily equivalent. Quantitative agreement between stochastic and MD dynamics for the long-time relaxation of supercooled liquids is well established [13], and MC simulations have been shown to be a very efficient way of studying glassy dynamics [12].

We now apply Eq. (7) to measure $\chi(t, t')$ after a sudden quench to very low temperature. Physical properties of the system now depend on the time t' spent since the quench, the system “ages” [14]. Energy slowly decreases with time, while dynamics gets slower [14]. The FDT in Eq. (3) no more applies, and the following generalization was suggested for glassy materials [15]

$$\frac{\partial}{\partial t'} \chi(t, t') = -\frac{X(t, t')}{T} \frac{\partial}{\partial t'} C(t, t'), \quad (8)$$

where $X(t, t')$ is the fluctuation-dissipation ratio (FDR), $X(t, t') = 1$ at equilibrium. Deviations of the FDR from unity may quantify the distance from equilibrium [15].

Earlier attempts to measure $X(t, t')$ in molecular glasses [7, 16] used the following protocol: quench the system at time 0; apply a small field at $t' > 0$ and measure $\chi(t, t')$ for times $t \geq t'$; build a parametric “FD plot” of $\chi(t, t')$ versus $C(t, t')$. Crucially, this amounts to replacing $\partial_{t'}$ by ∂_t in (8), a procedure which is correct if $X(t, t')$ is not an explicit function of t and t' [17]. Unbiased FDR measurements require instead the evaluation of $\chi(t, t')$ at fixed t for various t' , so that the FDR can be graphically deduced from the slope, $-X(t, t')/T$, of FD plots [18]. This is numerically too costly if nonequilibrium techniques are used. The difficulty is easily overcome with Eq. (7), and we shall therefore report the first unbiased FDR measurements in aging molecular liquids.

In Fig. 2 we use both time parametrizations to build FD plots in two glass formers: the LJ system described above

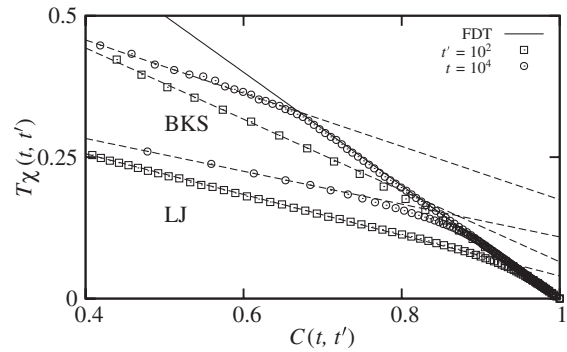


FIG. 2. Simultaneous measurement of $\chi(t, t')$ and $C(t, t')$ in aging LJ ($T = 0.4$, $k = 6.7$) and silica ($T = 2500$ K, $k = 2.7 \text{ \AA}^{-1}$). Fitting the nonequilibrium part of the FD plots (dashed line) for fixed- t parametrizations directly yields the FDRs $x = 0.29$ (LJ) and $x = 0.49$ (BKS). Incorrectly extracting x from fixed- t' data would yield 0.36 (LJ) and 0.63 (BKS), seriously underestimating FDT deviations.

and the BKS model for silica [19]. The LJ results are qualitatively consistent with earlier reports [16]. The plots consist of two distinct pieces, FDT being satisfied for small $t - t'$, “violated” for large $t - t'$. Strikingly, FD plots are well described by two straight lines, leading to a sensible definition of a constant FDR, x , at large $t - t'$. However, it is obvious in Fig. 2 that (incorrectly) estimating x from fixed- t' measurements yields values that seriously differ from unbiased estimates from fixed- t data, an error made in all previous works [16]. Both estimates only become equivalent if a nontrivial limiting FD plot is found at large time [15]. For silica, we find similar FD plots, and similar quantitative discrepancies between both time parametrizations. The disagreement with earlier results is more pronounced since FDR larger than unity were reported [7]. We have repeated our measurements at several temperatures between 500 and 2500 K, wave vectors from 0.3 to 13 \AA^{-1} , both for Si and O atoms. We always find FD plots as in Fig. 2 with $X(t, t') < 1$.

We have used the flexibility offered by Eq. (7) to characterize further the properties of FDRs in both aging liquids in Fig. 3. The top left panel presents evidence that different observables share the same FDR value, obtained by changing the wave vector used to evaluate dynamic functions. Similar results were obtained for silica. The top right panel shows that Si and O atoms in silica display similar FD plots, with equal FDR values. Again, we find similar results for the two types of particles in the LJ mixture. These results suggest that it is sensible to define, for fixed t , a *unique* FDR value $x(t)$ characterizing the nonequilibrium part of FD plots. These findings are therefore compatible with the physical idea [5] that slow rearrangements in aging supercooled liquids behave as if they were thermalized at an “effective temperature” defined by $T_{\text{eff}}(t) \equiv T/x(t)$ [15], with $T_{\text{eff}}(t) > T$ in the two investigated systems. Our data indicate that $T_{\text{eff}}(t)$ decreases very slowly with t . Finally, the bottom panel shows the tem-

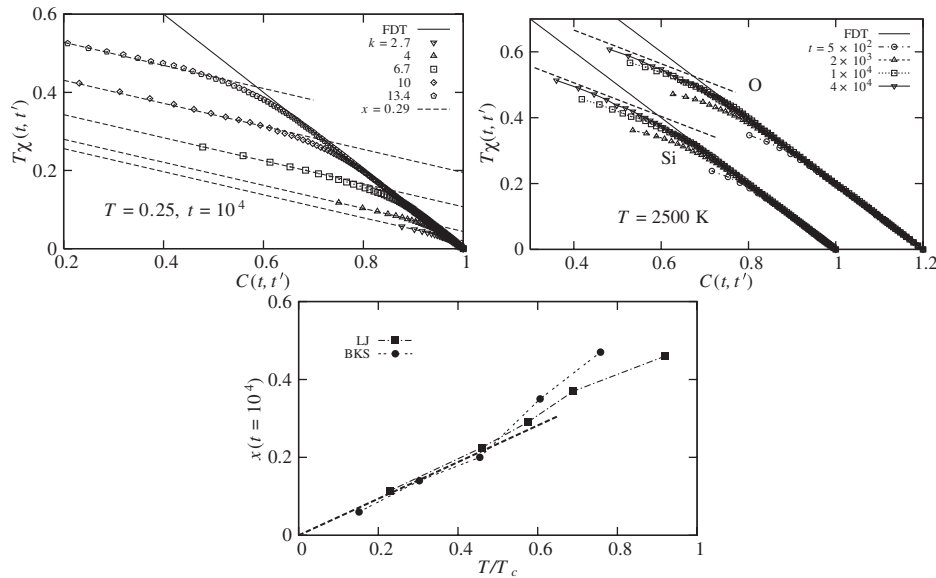


FIG. 3. Top left: FD plots for fixed T and t in the LJ system and different wave vectors displaying the same nonequilibrium value of the FDR. Top right: FD plots for Si and O (horizontally shifted by 0.2) in BKS for fixed T , $k = 2 \times 7 \text{ \AA}^{-1}$, and various t . For $t = 4 \times 10^4$, the FDR $x = 0.51$ fits both sets of data. Bottom: temperature dependence of the FDR at a single large time, $x(t = 10^4)$, for LJ and BKS systems. The temperature is normalized by the mode-coupling temperature T_c . A linear behavior (dashed line) is observed at low T .

perature dependence of the FDR measured at a single large time, $x(t = 10^4)$. To compare both liquids we have to normalize the temperature by some temperature scale. We choose the “mode-coupling” temperature [$T_c = 0.435$ (LJ) and $T_c = 3300$ K (BKS)] because equilibration is numerically difficult below T_c and aging effects can be detected. Remarkably, we find that FDRs in the two liquids display a very similar temperature dependence, $x \approx 0.47T/T_c$, at small T . This confirms that both fragile (LJ) and strong (BKS silica) glass formers studied in this work display similar aging properties.

We have introduced a new technique to efficiently measure linear susceptibilities in molecular simulations which uses unperturbed trajectories to evaluate response functions and outperforms subtraction techniques in Monte Carlo simulations. This allowed us to report the first unbiased numerical estimates of FDRs in aging molecular liquids and to extend its determination to a wide range of times, temperatures, and observables. We showed that previous analysis quantitatively underestimated FDT violations in LJ systems, while our results for silica are in qualitative disagreement with earlier results.

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