Fluctuation-dissipation relation in a sheared fluid

Jean-Louis Barrat[1] and Ludovic Berthier[1,2]

[1]*Département de Physique des Matériaux, Université Claude Bernard and CNRS, F-69622 Villeurbanne Cedex, France*
[2]*Laboratoire de Physique, ENS-Lyon and CNRS, F-69007 Lyon, France*

In a fluid out of equilibrium, the fluctuation-dissipation theorem (FDT) is usually violated. Using molecular dynamics simulations, we study in detail the relationship between correlation and response functions in a fluid driven into a stationary nonequilibrium state. Both the high temperature fluid state and the low temperature glassy state are investigated. In the glassy state, the violation of the FDT is similar to the one observed previously in an aging system in the absence of external drive. In the fluid state, violations of the FDT appear only when the fluid is driven beyond the linear response regime, and are then similar to those observed in the glassy state. These results are consistent with the picture obtained earlier from theoretical studies of driven mean-field disordered models, confirming the similarity between these models and simple glassy systems.

In the past years, a large body of theoretical [1], experimental [2] and numerical [3,4] work has been devoted to the study of correlation and response functions in nonequilibrium glassy systems. Generally, the nonequilibrium situation of interest is generated by a quench below the glass transition temperature. The system falls then out of equilibrium, in the sense that its relaxation time becomes far greater than the experimental time scale. Its properties therefore depend on the time t_w elapsed after the quench, also called waiting time. The most spectacular dependency is observed for the two-time correlation functions which depend then upon the two time arguments and not on the time difference only, as in an equilibrium system. These correlations decay with a relaxation time t_r that increases with t_w (aging), typically $t_r \propto t_w$. The same aging behavior is observed in the response functions, and a useful quantification of the nonequilibrium behavior is encoded in the way the usual equilibrium fluctuation dissipation theorem (FDT) is violated [5]. For atomic systems of the type studied in this paper, this violation has been shown by numerical studies to be similar to the one observed in high dimensional disordered mean-field models [4].

These studies, however, focus on the case of a nonequilibrium situation following a quench and on the subsequent aging phenomena. In Ref. [5], Cugliandolo *et al.* suggested another approach to nonequilibrium systems, in which the nonequilibrium state was generated by "stirring" the system. In such a situation, in which energy is fed into the system at a constant rate, the theory predicts that a stationary nonequilibrium state is reached, even when the unstirred system is in a glassy state: *aging is stopped* [5,6]. Further theoretical studies on driven mean-field disordered systems [7] established a detailed picture of the nonequilibrium behavior, which can be summarized as follows. The relaxation of these systems is a two-step process composed of a fast part which is essentially unaffected by the driving force, and a slow relaxation occurring on a time scale which is a decreasing function of the drive intensity. Simultaneously, a two-temperature pattern appears, the fast modes being equilibrated at the bath temperature T, while the slow ones have an effective temperature $T_{eff} > T$. Quantitatively, this is shown

by studying a correlation function $C(t) = \langle A(t_0+t)B(t_0) \rangle$ between two observables A and B, and the associated response function $\chi(t) = \delta \langle A(t_0+t) \rangle / \delta h(t_0)$, where h is the field conjugated to B. Whereas at equilibrium, these quantities are related by the FDT, $\partial_t C(t) = -k_B T \chi(t)$, this FDT has to be generalized in the driven system by introducing an effective temperature T_{eff}, through $\partial_t C(t) = -k_B T_{eff} \chi(t)$. In the limit of zero drive, one finds $T_{eff} \to T$ if $T > T_c$, (T_c is the temperature at which the relaxation time of the undriven system diverges) and equilibrium properties are recovered. For $T < T_c$, the limiting effective temperature coincides with that of the system *aging* at the same temperature [5,7]. In Ref. [8] it was shown that, for mean field models, T_{eff} is related to the configurational entropy available to the system near one free energy minimum, confirming the interpretation of T_{eff} as a true temperature [5,9], both in the thermodynamic and dynamical sense.

In this paper, we investigate the nonequilibrium situation created by a steady, homogeneous shear imposed on a simple glass forming liquid, i.e., a simple realization of the stirring systems considered in Ref. [5] which was suggested by Ref. [7]. Note however that, in practice, such a situation is more easily realized in a "soft" glassy system (a complex fluid with glassy behavior [10]), which can support homogeneous shear flow, than in a usual molecular glass, in which shear banding and fracture tend to take place. Simulations, on the other hand, allow to create an homogeneous shear even in a simple system. The goal of this paper is then to determine the behavior of a simple glassy system subjected to a shear and to compare the results with the main predictions of mean-field calculations, keeping in mind the possible relevance to soft glassy materials. Although the mean-field scenario is not *a priori* expected to apply to a three-dimensional fluid, it has the advantage of providing precise predictions, which can be compared easily to experimental or numerical results. Our focus will be on the fluctuation-dissipation relation, the general rheological properties already discussed by Yamamoto and Onuki [11] will be only briefly considered.

The system simulated in this work is a 80:20 mixture of 2916 Lennard-Jones particles, with interaction parameters that prevent crystallization [12]. In all the paper, the length,

energy and time units are the standard Lennard-Jones units σ_{11} (particle diameter), ϵ_{11} (interaction energy), and $\tau_0 = (m_1 \sigma_{11}^2 / \epsilon_{11})^{1/2}$ [13], where m_1 is the particle mass and the subscript 1 refers to the majority species [12]. The system has been described in detail elsewhere, and its equilibrium (high temperature) properties have been fully characterized. At the reduced density $\rho = 1.2$, where all our simulations are carried out, a ''computer glass transition'' is found in the vicinity of $T_c = 0.435$ and the slowing down of the dynamics seems to be described well by mode-coupling theory [12]. The aging behavior of the system below this temperature has also been characterized extensively, including the violation of the FDT in the glassy phase [14].

The homogeneous shear state corresponding to a planar Couette flow is obtained by using the SLLOD algorithm supplemented by Lees-Edwards boundary conditions [15]. The velocity gradient is in the z direction, and the fluid velocity in the x direction. Constant temperature conditions are ensured by thermostatting the velocities in the direction perpendicular to the flow using the Nosé-Hoover method [15], or in some cases through a simple velocity rescaling. The shear rate, denoted by $\dot\gamma$, naturally introduces a new time scale $\dot\gamma^{-1}$ into the problem. Obviously, a simulation involving a steady shear state is possible only if the available simulation time is significantly larger than $\dot\gamma^{-1}$. This limits our study to shear rates larger than typically $10^{-4}/\tau_0$, corresponding to 10^6 time steps. In molecular units, such shear rates are of course exceedingly large, as is usual in MD simulations. Much more reasonable values are obtained if units appropriate for colloidal systems are chosen instead.

The first important consequence of applying a shear to the system is that, in accordance with theoretical expectations, a nonequilibrium stationary state is reached after a transient of a few $\dot\gamma^{-1}$. This is true even at temperatures at which the corresponding undriven system behaves like a glass and does not reach equilibrium. The benefit is that many of the difficulties associated with the simulation of glassy systems, such as the dependence on the preparation method of the sample (especially cooling rate), are eliminated. At a given temperature, a sheared sample can be prepared either by cooling another sheared sample from a higher temperature, or by shearing a sample quenched at zero shear. The results will be identical provided the first steps of the simulation are discarded. That the time translation invariance property is recovered under shear is illustrated in Fig. 1, which displays the incoherent scattering function of a quenched and sheared sample for several different waiting times after the quench. As usual, the incoherent scattering function for the particles of type 1 and wave-vector $\mathbf{q}$ is defined by

$$C_{\mathbf{q}}(t) = \frac{1}{N_1} \sum_{j=1}^{N_1} \langle \exp(i\mathbf{q} \cdot [\mathbf{r}_j(t+t_0) - \mathbf{r}_j(t_0)]) \rangle. \quad (1)$$

In this study, only values of $\mathbf{q}$ in the y direction (i.e., perpendicular to both the velocity and the velocity gradient) will be considered. This choice avoids the complications due to convection by the average flow that arise for other wave vectors [11].
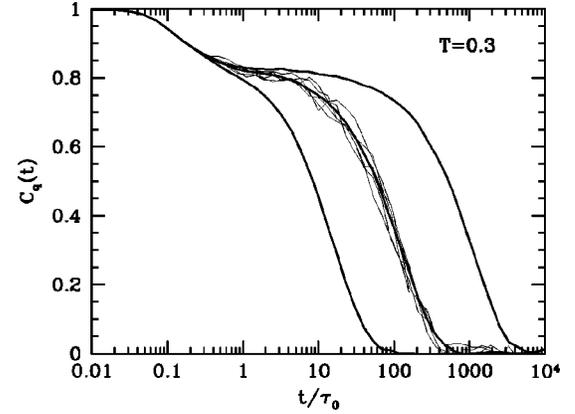
FIG. 1. Incoherent scattering functions for the A particles at $T = 0.3$ and $\mathbf{q} = 7.47\mathbf{e_y}$, the location of the main peak in the structure factor. Bold curves, from left to right: $\dot\gamma = 0.01$, 0.001, and 0.0001. For $\dot\gamma = 0.001$ five different two-time correlation functions, taken with time origins equally spaced during a run of duration $10^4\tau_0$ are also shown as light continuous curves. The absence of aging is illustrated by the fact that these curves coincide with the bold one.

In Fig. 1, it is clearly seen that the relaxation time t_r of the correlations is shear rate dependent. As already shown in Ref. [11], the viscosity η scales roughly as t_r. Consequently, η decreases when $\dot\gamma$ increases: this is a *shear-thinning* behavior. The viscosity is defined by $\eta(\dot\gamma) \equiv \sigma_{xz}(\dot\gamma)/\dot\gamma$, where σ_{xz} is the off-diagonal component of the stress tensor, and is shown in Fig. 2. The same type of rheological behavior was obtained in Ref. [11] for a similar system. A Newtonian regime, where η is independent of $\dot\gamma$, is obtained when $\dot\gamma^{-1} \gtrsim t_r$. For $T < 0.45$, no such regime is observable. The shear-thinning behavior is well characterized by a power law $\eta(\dot\gamma) \sim \dot\gamma^{-\alpha(T)}$. For the lowest temperature investigated here, $T = 0.3$, one finds $\alpha \approx 0.9$. This shear-thinning exponent is slightly smaller than the one obtained in [11]. There is, however, no reason to expect a universal value for α, which experimentally is found to be system dependent, with reported values between 0.5 and 1 [16].
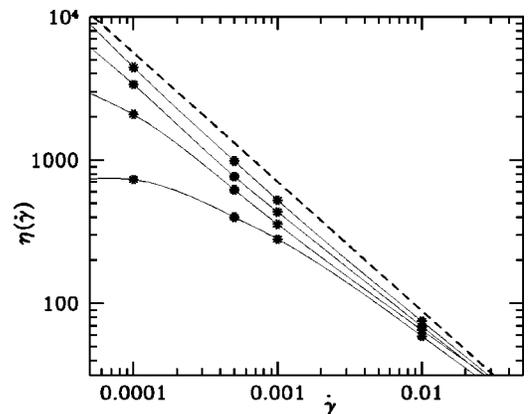
FIG. 2. Viscosity versus shear rate for temperatures (from bottom to top) $T = 0.5$, 0.45, 0.4, and 0.3. The solid lines are guides to the eye, the dashed line corresponds to a power law $\eta \propto \dot\gamma^{-0.9}$.

The fact that the time translation invariance is reestablished by shearing the system implies a superficial resemblance with equilibrium systems. The correlation function displayed in Fig. 1, for example, is very similar to the correlation functions in a fluid system slightly above the glass transition. In the following, the differences between the dynamics of fluctuations in the driven and equilibrium system is studied through the fluctuation-dissipation relation introduced in the introduction. In the present case, the two observables under study are $A_{\mathbf{q}}(t) = 1/N_1 \Sigma_j \epsilon_j \exp[i\mathbf{q} \cdot \mathbf{r}_j(t)]$, and $B_{\mathbf{q}}(t) = \Sigma_j \epsilon_j \cos[\mathbf{q} \cdot \mathbf{r}_j(t)]$, where ϵ_j is a random variable taken from a bimodal distribution $\epsilon_j = \pm 1$. It is straightforward to show that after averaging over the distribution $\{\epsilon_j\}$, the correlation function $\langle A_{\mathbf{q}}(t+t_0) B_{\mathbf{q}}(t_0) \rangle$ is equal to $C_{\mathbf{q}}(t)/2$, where $C_{\mathbf{q}}$ is the incoherent scattering function defined in Eq. (1). To compute the response function, a term $\Delta H = -h B_{\mathbf{q}}(t)$ is added to the Hamiltonian. The response function is then $\chi_{\mathbf{q}}(t) = \delta \langle A_{\mathbf{q}}(t+t_0) \rangle / \delta h(t_0)$. The procedure to study the FDT is then the following. The system is made stationary at a fixed temperature and shear rate. The field is switched on at t_0 and the observable $A_{\mathbf{q}}(t+t_0)$ is monitored. The same procedure is repeated for several (20 to 80) realizations of the charge distribution. This gives the integrated response function $M_{\mathbf{q}}(t)$, defined as

$$M_{\mathbf{q}}(t) = \int_{t_0}^{t+t_0} dt' \chi_{\mathbf{q}}(t') \simeq \frac{\langle A_{\mathbf{q}}(t) \rangle}{h}. \qquad (2)$$

The last equality holds in the linear response regime, that we carefully checked, by choosing a small amplitude for the field h (between 0.05 and 0.2). This procedure was carried out for four different values of the temperature ($T = 0.5$, 0.45, 0.4, and 0.3) both above and below the computer glass transition temperature. At each temperature, shear rates from 5.10^{-5} to 10^{-2} were considered. The wave vector was $\mathbf{q} = 7.47 \mathbf{e_y}$. The results are most easily analyzed by considering parametric plots of $M_{\mathbf{q}}(t)$ versus $C_{\mathbf{q}}(t)$. The slope of these curves is, by definition, $-k_B T_{\text{eff}}$.

In Fig. 3, such plots are shown for (a) $T = 0.3$, which is deep in the glassy region, and (b) $T = 0.5$, where the system is at equilibrium in the absence of shear. For $T = 0.3$, a very clear deviation from FDT is observed when the correlation falls below $C \simeq 0.8 = q$, which corresponds to the plateau value in the correlation functions (see Fig. 1). The parametric curve can be very well approximated by two straight lines, one with slope $-1/k_B T$ (FDT) at large correlations and one with a slope $-1/k_B T_{\text{eff}}$ for $C < q$. The latter slope saturates for the smallest shear rates to the value $T_{\text{eff}} \simeq 0.62 > T_c$ (this straight line correctly fits the two values $\dot{\gamma} = 0.001$ and 0.0001). Remarkably, this value for T_{eff} is very close (certainly within error bars) to the one obtained in Ref. [14], when studying the aging system. Such a coincidence was expected on theoretical grounds [5,7], and exemplifies the deep meaning of the effective temperature. As it is in fact a property of the free energy landscape available to the system, it naturally arises in both types of dynamics (aging and driven) of the system. The two-temperature pattern is also consistent with earlier expectations that a simple atomic
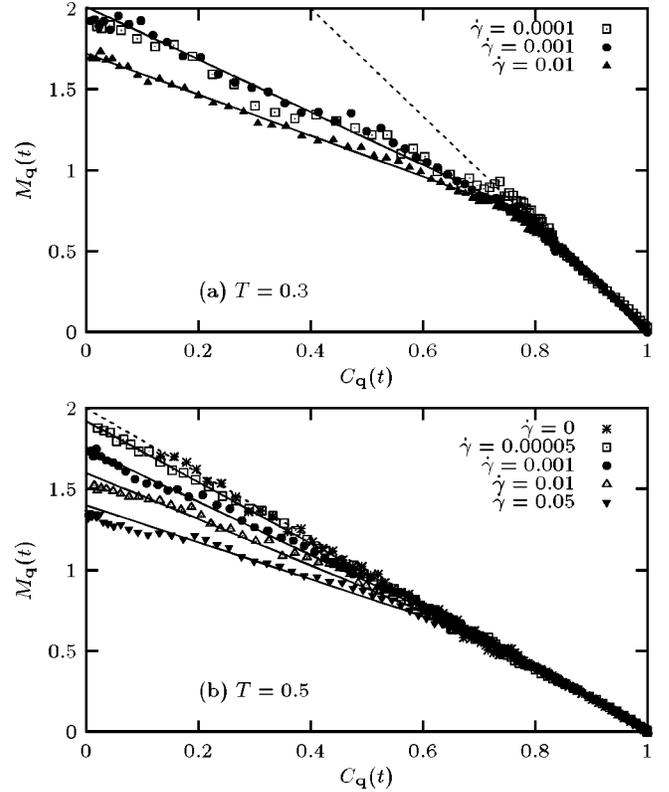
FIG. 3. Parametric plots for (a) $T = 0.3$ and (b) $T = 0.5$, and various shear rates. In both figures, the dashed line is the FDT, and has a slope $-1/T$. The full lines are linear fits to the data for $\dot{\gamma} > 0$.

glass has the same dynamical behavior of mean-field disordered models of the ''p-spin'' type ($p > 2$) [1,7]. It is worth noting that the value q below which the violation of FDT is observed is, again as expected from theory, approximately equal to the plateau value of the correlation functions. This had not been found in Ref. [14], and the present results show that this was probably due to preasymptotic effects in the aging results.

At $T = 0.5$, the FDT holds at zero shear [this is very well verified numerically, see Fig. 3(b)] and remains valid for small enough shear rates. Deviations are observed only for shear rates large enough to induce non-Newtonian behavior and shear-thinning. In this regime, it is natural to expect that deviations to FDT will become more important for increasing shear rates. The data clearly indicate that the parametric plot *can still be fitted by two straight lines*, with a shear rate dependent slope for the non-FDT part. If this slope is interpreted as an effective temperature, this temperature increases with increasing the strength of the driving force, which is a quite intuitive effect. Again, this is very similar to the results obtained in [7] for the disordered mean-field model. Finally, we note that the results obtained for $T = 0.4$ and $T = 0.45$ are similar to those obtained for $T = 0.3$ and $T = 0.5$, respectively.

In this paper, we have presented the first numerical study of the fluctuation-dissipation relation in a realistic model of a sheared fluid. This study demonstrates that the nonequilib-

rium fluctuations obey the *two-time scale, two-temperature scenario* which was previously derived for mean-field glass models [7]. Although the system is a three dimensional one, which will certainly differ from mean-field systems in many respects, the mean-field approach provides here a useful conceptual framework to rationalize the numerical findings. On short time scales, the fluctuation-dissipation temperature is equal to the microscopic temperature. As the driven system is forced to explore phase space further (slow relaxation), the correlation drops below its plateau value and a different fluctuation-dissipation temperature is observed, which is only weakly dependent on the bath temperature [7,14]. This last time scale is strongly shear rate dependent, as is well known from rheological experiments.

Our results were obtained on relatively short time scales, for a system which is usually accepted as a reasonable microscopic equivalent of molecular or metallic glasses. We believe, however, that they would be most easily applicable and experimentally testable for complex fluids, in which the glassy state can be more easily disrupted to establish a permanent shear flow.

[1] J.-Ph. Bouchaud, L.F. Cugliandolo, J. Kurchan, and M. Mézard, *Spin Glasses and Random Fields*, edited by A.P. Young (World Scientific, Singapore, 1998); T.R. Kirkpatrick and P.G. Wolynes, Phys. Rev. A **35**, 3072 (1987); T.R. Kirkpatrick and D. Thirumalai, Phys. Rev. B **36**, 5388 (1987).

[2] R.L. Leheny and S. Nagel, Phys. Rev. B **57**, 5154 (1998); N.E. Israeloff and T.S. Grigera, Europhys. Lett. **43**, 308 (1998); Phys. Rev. Lett. **83**, 5038 (1999); D. Bonn, J. Tanaka, G. Wegdam, H. Kellay, and J. Meunier, Europhys. Lett. **45**, 52 (1999); L. Bellon, C. Laroche, and S. Ciliberto, e-print cond-mat/9906162.

[3] W. Kob and J.-L. Barrat, Phys. Rev. Lett. **78**, 4581 (1997); W. Kob, F. Sciortino, and P. Tartaglia, Europhys. Lett. **49**, 590 (2000).

[4] G. Parisi, Phys. Rev. Lett. **79**, 3660 (1997); J.-L. Barrat and W. Kob, Europhys. Lett. **46**, 637 (1999); R. Di Leonardo, L. Angelani, G. Parisi, and G. Ruocco, Phys. Rev. Lett. **84**, 6054 (2000).

[5] L.F. Cugliandolo, J. Kurchan, and L. Peliti, Phys. Rev. E **55**, 3898 (1997).

[6] H. Horner, Z. Phys. B: Condens. Matter **100**, 243 (1996); L.F. Cugliandolo, J. Kurchan, P. Le Doussal, and L. Peliti, Phys. Rev. Lett. **78**, 350 (1997).

[7] L. Berthier, J.-L. Barrat, and J. Kurchan, Phys. Rev. E **61**, 5464 (2000).

[8] S. Franz and M. Virasoro, J. Phys. A **33**, 891 (2000).

[9] T. Nieuwenhuizen, Phys. Rev. Lett. **80**, 5580 (1998).

[10] P. Sollich, Phys. Rev. E **58**, 738 (1998).

[11] R. Yamamoto and A. Onuki, Phys. Rev. E **58**, 3515 (1998).

[12] W. Kob and H.C. Andersen, Phys. Rev. E **53**, 4134 (1995); **51**, 4626 (1995); Phys. Rev. Lett. **73**, 1376 (1994).

[13] Note that in previous works [12,14], a different time unit, $\tau = (m_1 \sigma_{11}^2/48\epsilon_{11})^{1/2}$, is sometimes used when dealing with Lennard-Jones particles.

[14] W. Kob and J.-L. Barrat, Eur. Phys. J. B **13**, 319 (2000).

[15] M. Allen and D. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).

[16] R.G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, New York, 1999).