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Ageing, rheology and effective temperature in a glass-forming system

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Abstract
In this paper, I review some of the recent results obtained, using molecular dynamics simulations, on the out-of-equilibrium behaviour of glass-forming systems. Both the ageing (evolution after a fast quench in the glassy phase) and the driven (evolution under uniform shear flow) situations are considered. The theoretical concept of effective temperature that was shown to characterize such nonequilibrium states well is also discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In textbooks, the description of glassy systems is often limited to that of simple molecular glasses, such as silica, or polymeric glasses. In the last ten years, however, it has become increasingly evident that a much broader conception of 'glassy' behaviour could be fruitful. In some sense, all systems that do not explore their phase space in a (quasi-) ergodic manner can be considered as glassy, in the sense described for example in the classic book by Ma [1]. Glassiness, in that sense, is indeed a matter of timescales, not of molecular structure. This has recently prompted many researchers to investigate 'glassiness' in systems as diverse as foams, emulsions, colloidal pastes, and granular media, which share the property of having a relaxation time τ longer than, or comparable to, the experimental timescales [2].

Another important outcome of theoretical, experimental, and numerical work in the last ten years is the understanding that the *nonequilibrium* behaviour of such glassy systems could be usefully discussed and described within a statistical physics perspective. Although nonequilibrium systems have been widely studied in material sciences and rheology, notions from statistical physics—such as correlation and response functions—have seldom been used in the field.

In this paper, I will review some of these efforts, putting particular emphasis on results that were obtained using numerical approaches in the field of liquids, and on the theoretical framework provided by the 'mean-field' or 'mode-coupling' theories [3]. I will only refer much more briefly to the equally important 'soft glassy rheology' and 'potential energy landscape' approaches, which are undergoing parallel development.

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Conceptually, and even practically, nonequilibrium behaviour is observed in two typical situations. The first one is where the material, whose relaxation time is very long (in some cases, essentially infinite), is simply left to *age* after modifying some external parameter (e.g. temperature, pressure) or after preparation in some initial state (foams, grains, colloids). The corresponding *ageing* phenomena are characterized by a very slow drift of thermodynamic quantities such as energy or volume, but also by much more spectacular changes in the responses to a time-dependent stimulus. These changes, which have been widely investigated by materials scientists (in particular for polymeric glasses) [4], received much more attention from physicists in the context of spin glasses, and their interpretation prompted the development of several theoretical approaches in the 1990s.

The second practical way of creating a nonequilibrium situation is to *drive* the system through the application of some external field or force, which feeds energy into the system on large scales. The commonest example of such a drive is simple shear, which is routinely used to study the rheological properties of complex fluids. The drive may be oscillatory or permanent, and in the following we will concentrate on the latter case. A simple dimensional analysis suggests that the shear rate γ, which has the dimension of a frequency, should be combined with the relaxation time τ to form the so-called Deborah number $De = \gamma\tau$. Investigating systems with a large relaxation time implies a large range of Deborah numbers, in particular the possibility of having a large De without using exceedingly large shear rates. The separation of timescales between a large relaxation time and the 'microscopic' relaxation times is of course the crucial ingredient here.

As many of the results discussed in this paper are obtained from classical molecular simulations (mostly based on molecular dynamics, but there is little doubt that Brownian dynamics or kinetic Monte Carlo dynamics would lead to similar results), it is appropriate to briefly discuss here what we mean by 'long times'. In our view, there are two essential points that can be taken as characterizing glassy behaviour: the fact that the relaxation time becomes comparable to the 'experimental' timescale, and the fact that the relaxation time is well separated from the microscopic (vibrational) timescale. In computer simulations, the 'experimental' scale is of course much shorter than in laboratory experiments, but with present-day computers a very reasonable timescale separation can be achieved with microscopic scales—by typically 5–6 orders of magnitude—so one can reasonably hope to get some insight into 'glassy' behaviour by using such simulations. Obviously not all dynamical processes are within the reach of computer simulations—e.g. crossing high energy barriers is not possible on the timescales under consideration—but an interesting phenomenology is nevertheless expected.

The paper is organized as follows. I will first recall some of the theoretical background, then the main results obtained from computer simulations on ageing and driven systems; a short section will be devoted to the concept of effective temperature.

2. Theoretical background

Two broad classes of models have been proposed to describe the phenomenology of ageing and driven glassy systems. The first class, developed in particular by Bouchaud and co-workers [5], is that of 'trap models' and the associated 'soft glassy rheology' [6]. Briefly speaking, the idea is to describe the system as a point evolving in a complex energy landscape. This point gets trapped in energy minima, and escapes from these minima with a rate given by an Arrhenius law. The correlation functions of the model can then be entirely specified by the distribution of energy minima. When this distribution is exponential, of the form $p(E) \sim \exp(-\alpha E)$, the resulting escape times become broadly distributed (no first moment) when the inverse

temperature $\beta > \alpha$. As a result, the system cannot equilibrate for such low temperatures, and ageing phenomena are observed.

The generalization of this picture to driven systems, as proposed in [6], consists in introducing an extra dependence of the trap depths on a parameter ℓ that describes the 'state of strain' of the system. In simple shear, ℓ grows linearly with time and adds a quadratic energy to the trap depth, i.e. $-E \to -E + k\ell^2/2$. The larger the strain, the easier the escape from the trap. After escaping the strained trap, the system falls again at random into an *unstrained* trap chosen at random. This 'soft glassy rheology' model is quite simple (in the sense that the probability $P(E, \ell, t)$ in the energy–strain space obeys a simple rate equation, but still leads to a number of nontrivial predictions for the (linear and nonlinear) rheological behaviour. These predictions are reviewed in [6], and have been used to rationalize a number of experimental findings on complex fluids (see e.g. [7]).

The second class of models, originally developed in the context of spin glasses, is based on the fact that some disordered spin systems can be solved in the mean-field (infinite-dimension) limit. Interestingly, these systems can be shown (in the mean-field limit) to undergo a transition from an ergodic state to a nonergodic one at some finite temperature T_d, similar to the glass transition predicted by the 'mode-coupling' theories of liquids [8, 9]. Below T_d, these systems display ageing, in the sense that correlation functions of the type $C(t, t') = \langle A(t')A(t)\rangle$ depend both on the time $t = t_w$ (waiting time) spent in the glass phase and on the time difference $\tau = t' - t$. Some properties of the ageing correlation functions can be calculated essentially exactly. In particular, it can be shown that, in the long-waiting-time limit, correlation functions C and their associated response functions R obey a generalization of the equilibrium fluctuation dissipation theorem, which can be written as

$$R(t, t') = X(C)\frac{\partial C(t, t')}{\partial t}. \tag{1}$$

The function $X(C)$ is called the fluctuation dissipation ratio (FDR). Such relations are most conveniently displayed in the form of a parametric plot [10] in which the integrated response following a step in the field at t_w (or susceptibility), $M(t_w, t_w + \tau) = \int_{t_w}^{t_w+\tau} R(s, t_w + \tau)\,\mathrm{d}s = \int_{C(t_w,t_w+\tau)}^{C(t_w,t_w)} X(C)\,\mathrm{d}C$ is plotted as a function of the correlation. In such a plot, the existence of an asymptotic limit is easily proved by checking that a collapse of the curves obtained for different values of t_w occurs, and that the FDR is the slope of the limiting curve. In equilibrium, this slope is just the inverse of the thermodynamic temperature. This allowed the authors of [11] to introduce the notion of an effective temperature associated with the FDR, which will be discussed in more detail in section 4.

Generalizing this type of model to a 'driven' situation can be achieved by adding to the equations of motion for the spins a term that cannot be derived from a Hamiltonian, therefore violating the detailed balance conditions. This was done in [12], and we briefly summarize here the main results obtained in this reference, for a simple system (the 'p-spin' mean-field model), studied under conditions that involved a constant energy input from an external driving force, analogous to the effect of shear on a fluid. The resulting stationary nonequilibrium state was studied as a function of the external drive (the intensity of which will be denoted by ϵ) and temperature T.

For $\epsilon = 0$, the model has an ideal glass transition (diverging relaxation time) at a finite temperature T_c. For $T > T_c$, the correlation functions are described by mode-coupling-like differential equations, and display the characteristic two-step relaxation predicted by these equations. Below T_c, the system cannot equilibrate, and displays 'ageing' behaviour.

Under a finite external drive ($\epsilon \neq 0$), the system is stationary at all temperatures. For $T < T_c$, and in the asymptotic limit $\epsilon \to 0$, the correlation functions retain the characteristic

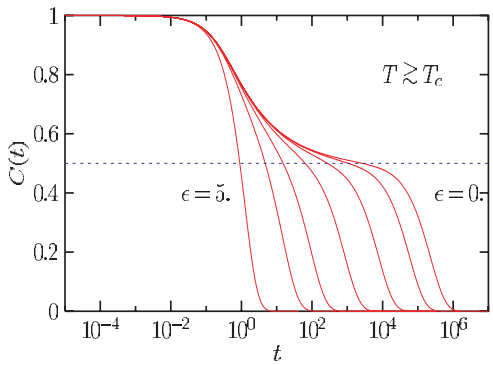

Figure 1. 'Shear thinning' of the correlation function in the p-spin model under an external drive. The decay of the spin–spin correlation function (here at T slightly above T_c) is accelerated by the external drive.

two-step shape of the equilibrium system, with an α-relaxation time that depends on γ. For $T < T_c$, this relaxation time diverges as $\gamma \to 0$, while for $T > T_c$ it goes to its equilibrium value in this limit.

On the basis of a power dissipation argument, we were able, for this simple system, to define quantities equivalent to the viscosity η and shear rate γ in a fluid under shear. This 'viscosity' was found to have a characteristic shear thinning behaviour, with a shear thinning exponent equal to $-2/3$ for $T > T_c$. For $T < T_c$, the viscosity diverges as $\gamma \to 0$, and the shear thinning exponent appears to depend on temperature.

The behaviour of the FDR was also investigated as a function of T and γ. In a system invariant under time translation, the relation for the FDR is of the form given by

$$R(t) = -\frac{X(C)}{k_B T}\frac{\mathrm{d}C}{\mathrm{d}t}. \tag{2}$$

Here $R(t)$ and $C(t)$ are, respectively, a response function and the associated correlation function. In equilibrium, the fluctuation dissipation theorem can be written as $X(C) = 1$. In the sheared system, the FDR is found, for $T < T_c$, to be a discontinuous function of C in the limit $\gamma \to 0$. For $C > q$, the Edwards–Anderson parameter $X(C) = 1$, while for $C < q$, $X(C) = m < 1$, indicating the existence of an *effective temperature* larger than the bath temperature for long timescales [11]. At finite shear $\gamma \neq 0$, the FDR also has an almost discontinuous behaviour as a function of C. For $T > T_c$, the discontinuity decreases and vanishes when $\gamma \to 0$, so equilibrium behaviour is recovered in this limit.

These results are summarized in figures 1 and 2.

3. Some results from simulations

3.1. The model

The system simulated in our work is an 80:20 mixture of Lennard-Jones particles, with interactions

$$V(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{3}$$

(i and j refer to the two species A and B) and interaction parameters that prevent crystallization [13]. Throughout the paper, the length, energy, and time units are the

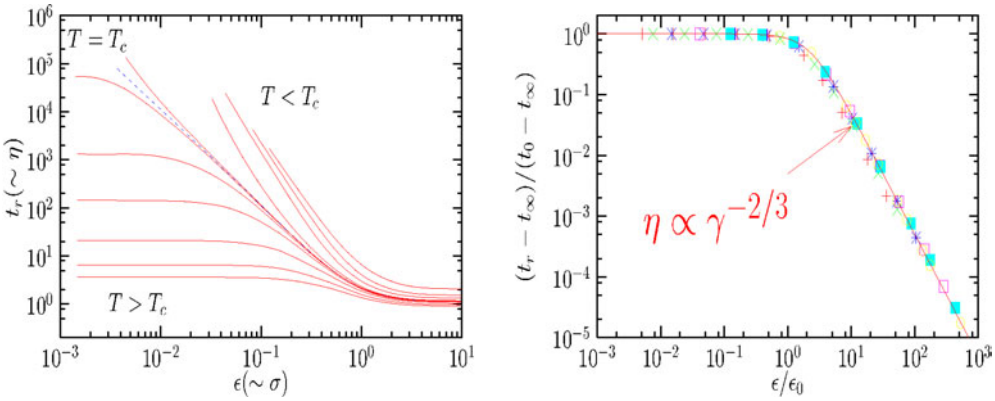

Figure 2. Left panel: 'viscosity' (proportional to the relaxation time) versus 'shear rate' in the p-spin model under an external drive. Right panel: the same result for $T < T_c$, rescaled to demonstrate that the shear thinning exponent is 2/3.

standard Lennard-Jones units σ_{AA} (particle diameter), ϵ_{AA} (interaction energy), and $\tau_0 = (m_A\sigma_{AA}^2/\epsilon_{AA})^{1/2}$, where m_A is the particle mass and the subscript A refers to the majority species. Particles have equal masses, and the interaction parameters are $\epsilon_{AB} = 1.5\ \epsilon_{AA}$, $\epsilon_{BB} = 0.5\ \epsilon_{AA}$, $\sigma_{BB} = 0.88\ \sigma_{AA}$, $\sigma_{AB} = 0.8\ \sigma_{AA}$. With these parameters for interactions between species, the equilibrium (high-temperature) properties of the system 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 [13].

3.2. 'Ageing' in a computer simulation

The first studies of this model under nonequilibrium conditions of the ageing type were presented in [15]. The simulation procedure consisted in quenching the system to a low temperature, and monitoring the evolution of the correlation and response functions as a function of the waiting time t_w (time elapsed after the quench). The correlation function under consideration is the self-part of the dynamical structure factor, denoted by C_k, and the associated integrated response function M_k is obtained by applying a sinusoidal field to tagged particles. The essential results, illustrated in figures 3 and 4, are that the correlation functions 'age' typically with a relaxation time that increases with t_w as t_w^α (α close to unity), and that the response and correlation are linked by a relation similar to that predicted for simple mean-field spin glass models, i.e. a 'two-temperature' relation, in which the FDT plot is essentially constituted by two straight lines. These results [14, 15], which confirm the close relation between spin glass models undergoing 'one-step' replica symmetry breaking and structural glasses, have been confirmed by a number of simulation studies.

3.3. Driving a glassy system with an external shear

The same system can be subjected to an external drive by imposing a uniform shear flow through Lee–Edwards boundary conditions [16, 17]. The first spectacular effect is the shear thinning effect [17] illustrated in figures 5 and 6. Remarkably, this shear thinning is quite close to the one predicted by mean-field theories, in that the high-shear-rate behaviour can be fitted

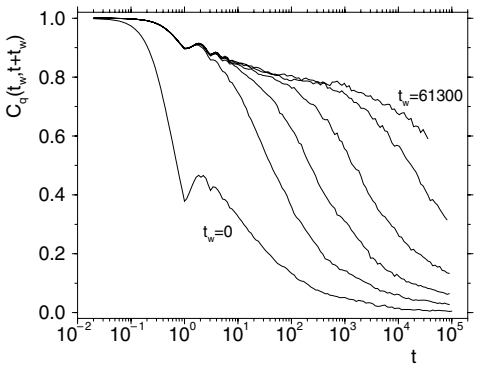

Figure 3. $C_k(t_w + \tau, t_w)$ after a quench to $T = 0.3$, for various values of the waiting time t_w.

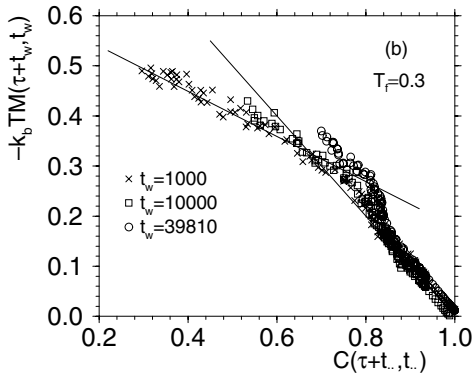

Figure 4. A parametric plot of integrated response versus correlation at $T = 0.3$; the different symbols correspond to different waiting times, and the straight lines have slopes corresponding to the equilibrium FDT $(1/0.3)$ at large values of C and $1/0.65$ at small C.

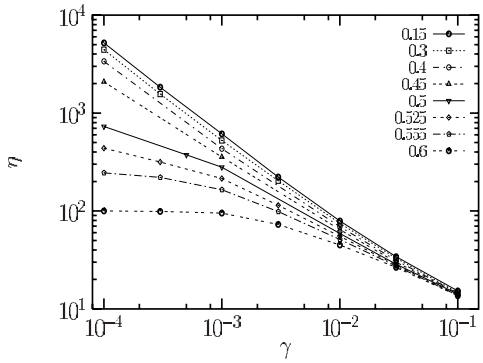

Figure 5. Viscosity versus shear rate for different temperatures in the range $T = 0.15$–0.6. The different symbols refer to different temperatures (indicated in the figure). Note the similarity with figure 2.

with a power law $\eta(\gamma) \sim \gamma^{-\alpha}$, with $\alpha \simeq 2/3$. In the glass phase, the behaviour appears to be close to a yield stress fluid, $\sigma = \sigma_0 + A\gamma^{\alpha}$. This shear thinning is also seen in the correlation functions (figure 7).

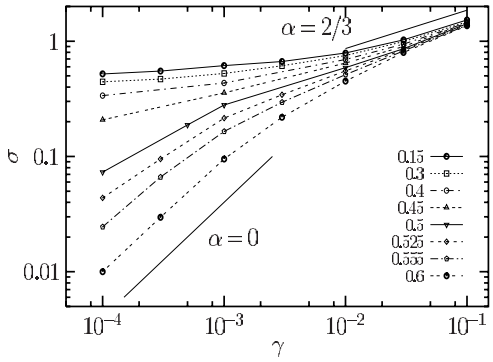

Figure 6. The same data as in figure 5, plotted in the form of flow curves (shear stress versus shear rate). At low shear rates and low temperatures, the stress seems to level off at a finite value, indicating a yield stress fluid.

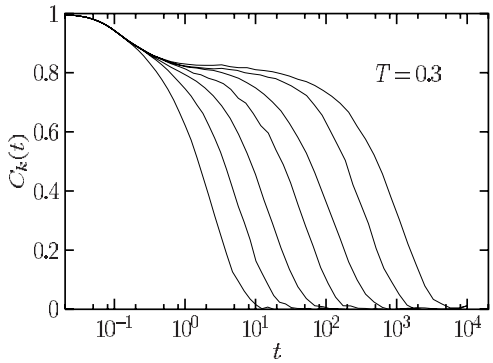

Figure 7. $C_k(t)$ at $T = 0.3$ and various values of the shear rate. Note the similarity with figure 1.

The next step is to measure response functions, as for the ageing systems. Again, a 'two-temperature' plot is found. In this case, it was shown that the same slopes (i.e. the same FDRs) are obtained for many different pairs of response/correlations associated with various observables, as illustrated in figure 8.

4. The fluctuation dissipation ratio and effective temperature

As indicated in the introduction, the FDR can be interpreted as the inverse of an effective temperature. The 'two-temperature' scenario which appears to be obeyed by structural glasses corresponds to an equilibration of fast degrees of freedom with the external temperature, while slow degrees of freedom are out of equilibrium and have response properties equivalent to that of a system at a higher temperature. To illustrate this picture physically, we have realized a numerical experiment in which a 'thermometer', in the form of heavy tracer particles, was coupled to the system. Because we have chosen large masses, we can adjust the Einstein frequency of the tracer particles to values larger than the structural relaxation time, with the result that the particles are effectively coupled to slow degrees of freedom. The average kinetic energy of the tracers then provides a measure of the 'temperature' associated with the slow degrees of freedom, and is found to be equal to the value that would be predicted from the second slope of the fluctuation dissipation plot (see figure 7).

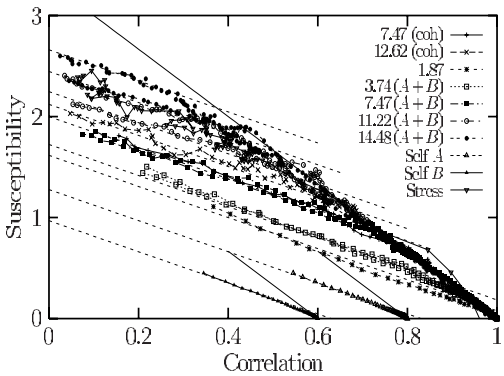

Figure 8. A parametric plot of the integrated response at $T = 0.3$ and $\gamma = 10^{-3}$. The different symbols correspond to different observables, including in particular: coherent and incoherent dynamical structure factors at various wavevectors (indicated in the figure), the off-diagonal stress tensor, and the diffusivity (see [17] for details). The full line is the equilibrium FDT of slope $-1/0.3$; the dashed lines have slope $-1/0.65$.

A physical interpretation of the two-temperature scenario in terms of the so-called 'potential energy landscape' picture has been given in [18, 19]. Within this picture, the system evolution takes place on two timescales: on a short timescale the system essentially vibrates around a fixed configuration in phase space, while on longer timescales it evolves between configurations. The free energy can therefore be separated into configurational and vibrational parts, and a different temperature is associated (through the usual thermodynamic formulation $\partial S/\partial F = 1/T$) with each contribution. In nonequilibrium situations with two widely separated timescales for evolution, the two temperatures (vibrational and configurational) are different. By generalizing the reasoning that leads to the equilibrium fluctuation dissipation theorem, it may be shown that each temperature will govern the FDR on the associated timescale. This picture was verified quantitatively in [19] for ageing systems, but remains to be confirmed for driven systems, in which some approximations made (such as the harmonic approximation for computing vibrational contributions) may be doubtful.

5. Conclusions, perspectives

The picture that emerges from the simulations is, broadly speaking, consistent with the theoretical picture developed throughout the last decade, based on the analogy between the mode-coupling equations [8] and the mean-field description describing disordered systems [9]. This agreement is satisfactory, in the sense that this scenario provides the first rigorous statistical mechanical treatment that encompasses essentially all the phenomenology of glass-forming liquids. The thermodynamic consequences of this scenario have been explored in much detail, up to quantitative comparison with simulation data [20]. However, it is important to realize the limitations of this approach, which—like early mode-coupling theories—is unable to account for the activated processes surmounting finite barriers that probably govern the relaxation of many molecular systems in the vicinity of the experimental glass transition temperature. In this respect, colloidal systems may be closer to an experimental realization of this theoretical scenario. The fact that results of molecular simulations are apparently in good agreement with this scenario may be related to their strong limitations as far as the exploration of timescales is concerned.

The strength of the theoretical picture, on the other hand, is in defining precise concepts that can be probed in experiments, such as the effective temperature idea based on the FDR. Such concepts are likely to retain their importance beyond mean-field theory, and some experiments have started to test their applicability [21, 22] for ageing systems. Another important aspect is the link with mode-coupling theories of liquids, with the possibility of using such techniques—that allow one to use the available information on the structure of the fluid—to study e.g. rheological problems within a rigorous statistical physics framework [23].

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