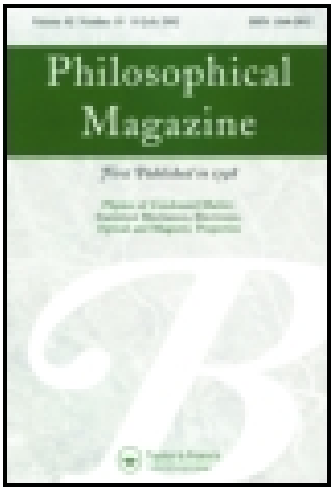

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Silvio Franz [a] , Claudio Donati [b c] , Giorgio Parisi [c] & Sharon C. Glotzer [b]

[a] The Abdus Salam International Centre for Theoretical Physics , Strada Costiera 11, PO Box 563, 34100, Trieste, Italy

[b] Center for Theoretical and Computational Material Science, and Polymers Division, National Institute of Standards and Technology , Gaithersburg, Maryland, USA

[c] Università di Roma 'La Sapienza' , P.le A. Moro 2, 00185, Rome, Italy

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On dynamical correlations in supercooled liquids

SILVIO FRANZ†||, CLAUDIO DONATI‡§, GIORGIO PARISI§
and SHARON C. GLOTZER‡

† The Abdus Salam International Centre for Theoretical Physics,
Strada Costiera 11, PO Box 563, 34100 Trieste, Italy
‡ Center for Theoretical and Computational Material Science, and Polymers
Division, National Institute of Standards and Technology, Gaithersburg,
Maryland, USA
§ Università di Roma 'La Sapienza', P.le A. Moro 2, 00185 Rome, Italy

ABSTRACT

We show how the growth of a dynamical correlation length and its associated susceptibility recently observed by the present authors and co-workers as T_c is approached can be understood in an appropriate theoretical framework. We discuss some predictions for these quantities in the region below T_c which have not yet been explored in numerical simulations.

One of the most striking features of the physics of supercooled liquids and glasses is the high degree of universality underlying the glass transition, and the scaling laws characterizing the 'avoided' dynamical phase transition described by the mode-coupling theory (Goetze 1989). Since the work of Kirkpatrick and Thirumalai (1987) and Kirkpatrick and Wolynes (1987a,b), we know that many of the fundamental features of glass physics are captured by a certain class of simple generalized spin-glass models. These are models described by a Hamiltonian $H[\mathbf{S}]$ which is a random Gaussian function of an extensive number of spin variables $\mathbf{S} = \{S_i\}$, $i = 1, \ldots, N$, which can be real, Ising, Potts, etc., variables. Since the general features of these models are largely independent of the nature of the variables involved, it has become customary to consider *spherical models*, where the S_i are real and subject to the constraint $\sum_i S_i^2 = N$ such that the configuration space is an N-dimensional sphere of radius $N^{1/2}$. This choice allows for important simplifications in the analytic treatment of the model, and we restrict our discussion here to this simplified model. The physics of this model depends on the range of the correlation function $\overline{H[\mathbf{S}]H[\mathbf{S}']}$, which is usually taken to be a function of the overlap $q(\mathbf{S}, \mathbf{S}') = (1/N)\sum_i S_i S_i'$, that is

$$\overline{H[\mathbf{S}]H[\mathbf{S}']} = f(q(\mathbf{S}, \mathbf{S}')). \tag{1}$$

The function $f(q)$ is an increasing function of q; the more similar the two configurations, the more correlated the energies are. If the correlations decay rapidly enough (faster than q^2), the physics of the model display many features in common with supercooled liquids and glasses (Mezard and Parisi 1990, Nieuwenhuizen 1995). The case $f(q) = q^p$ is known as p-spin model. The various aspects of glassy

|| E-mail: franz@ictp.trieste.it.

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phenomenology can be studied exaclty within these simple mean-field models. At a high temperature T, the dynamics of this model are described by an equation of motion identical with the schematic mode coupling equation (with the appropriate memory kernel) and exhibits, for example, both α and β relaxations, a dynamical transition at a temperature T_c, and a power law divergence of the relaxation time. The study of the statics on the other hand reveals that below T_c, where ergodicity is broken, the partition function is dominated by an exponentially large number of ergodic components with similar macroscopic characteristics. The logarithm of this multiplicity is identified with the configurational entropy Σ. This quantity decreases for decreasing T and goes to zero at a finite temperature T_k in a fashion similar to that predicted by the Gibbs–Di Marzio (1958) entropy crisis.

The success of mean-field spin-glass models in describing many features of liquid–glass physics leads to the conjecture that many of the characteristics of fragile glass formers can be ascribed to universal properties of random or quasirandom manifolds (energy landscapes) in a high dimensional (configuration) space. The application to real (finite-dimensional) systems supposes that while the structure of metastable states can be similar to that found in the mean-field model, the barrier heights (which diverge with the volume in the mean field theory) are finite in real systems. This explains the fact that the sharp dynamical transition becomes just a cross-over in real liquids. According to the mean-field theory, ergodicity breaks down at T_c. On approaching T_c from above, two time scales (β and α), corresponding to 'local' relaxation and 'diffusion', develop and become increasingly separated, and the α time scale eventually diverges at T_c. A useful picture to visualize the situation in phase space could be that of a particle which is free to move rapidly inside a 'cloud'. The cloud itself diffuses in configuration space, but at a much slower speed. The temperature T_c is the temperature below which the motion of the clouds is completely stopped. Beyond the mean-field theory, the clouds are mobile even below T_c.

In this paper we show how this mean-field picture can help us to interpret recent numerical results on Lennard-Jones liquids (Kob *et al.* 1997, Bennemann *et al.* 1999, Donati *et al.* 1999a,b) which have shown the existence of a dynamical correlation length that grows as the temperature T_c is approached from above, while the static correlation length remains small at all temperatures.

Since density fluctuations 'freeze' at the liquid–glass transition, one often considers the generalized Edwards–Anderson parameter function $\int \mathrm{d}x \langle \delta\rho(x) \rangle \langle \delta\rho(y+x) \rangle$. The growth of the correlation length can be detected by studying the order parameter fluctuations, which as shown by Donati *et al.* (1999a,b) is related to the volume integral of the four point function $\langle \delta\rho(x)\delta\rho(y) \rangle^2 - \langle \delta\rho(x) \rangle^2 \langle \delta\rho(y) \rangle^2$. The growth of the length associated with the point function was first envisaged in liquids by Dasgupta *et al.* (1991). These order parameter functions involve an infinite number of variables. One can reduce the number of variables from infinity to one by considering, in analogy with spin systems, measures of the 'overlap'. A useful definition of the overlap between two configurations with particle coordinates $X = \{x_1, \ldots, x_N\}$ and $X = \{y_1, \ldots, y_N\}$ is

$$q(X, Y) = \int \mathrm{d}x \, \mathrm{d}y \, w(x - y) \rho_X(x) \rho_Y(y), \tag{2}$$

where ρ_Z is the microscopic density corresponding to configuration $Z = X, Y$ and $w(r)$ is a short-range mask function close to one at distances smaller than some

fraction (e.g. 0.3) of the particle radius and close to zero above that distance. With this overlap we can associate a susceptibility as

$$\chi = \langle q^2(X, Y)\rangle - \langle q(X, Y)\rangle^2. \tag{3}$$

If we consider the equilibrium average, the distribution of X and Y would just be the product $1/Z^2 \exp\{-\beta[H(X) + H(Y)]\}$. We shall be interested in the case in which the equilibrium average is dominated by an exponentially large number of metastable states, each one carrying vanishing weight.

The interpretation that we would like to give of the dynamical length is that, with reference to the above pictorial image, correlations inside the cloud are high and grow as T_c is approached both from above and from below, while the correlations between different regions of the phase space the cloud explores are regular and small at all temperatures.

We use the method of the effective potential approach to the glass transition, which provides us with useful recipes to deal with metastable states. This approach has been discussed elsewhere and will not be reviewed here (Franz and Parisi 1997, 1998, Mézard 1998). The basic quantity of the theory is a constrained free energy, in which only the configuration with a fixed overlap q with an equilibrium (but otherwise random) reference configuration is taken into account:

$$V(q) = \frac{1}{Z}\int \mathrm{d}Y \exp[-H(Y)] \log\left(\int \mathrm{d}X \exp[-H(X)]\delta[q(X, Y) - q]\right). \tag{4}$$

Note that the average over the configuration Y is similar to the quenched average usually performed in disordered systems. In these systems, $V(q)$ is a self-averaging quantity. This restricted free energy allows the system to explore portions of the configuration space having vanishing canonical probability, and which are responsible for dynamical 'freezing'. We shall be interested in the situation in which an exponentially large number of metastable states contributes to the unconstrained free energy. In this situation, the equilibrium average of $q(X, Y)$ and the corresponding correlation function will be dominated by configurations X and Y belonging to different metastable states. In the potential (4) instead, if we properly tune the value of the parameter q, we can study a correlation function in which X and Y belong to the same metastable state. Indeed, while for $T > T_c$ the potential is a growing function of q with a single minimum at low q, at T_c a secondary minimum appears. The primary minimum corresponds to the whole free energy, where one is summing over all the configurations X and Y in different metastable states. The secondary minimum corresponds to having X and Y in the same state. Indeed, the value of q in the primary (low q) minimum represents the overlap between typical configurations belonging to different metastable states, while the value of q in the secondary minimum represents the overlap between typical configurations belonging to the same metastable state. Correlation functions computed with the value of q corresponding to the primary minimum are ordinary Gibbs averages, while correlation functions computed with the value of q^* corresponding to this minimum correspond to configurations belonging to the same metastable state. In particular, the two averages for the overlap susceptibility can be computed as the inverse curvature of the minima:

$$\chi = \frac{1}{V''(q)|_{q=q_{\min}}}. \tag{5}$$

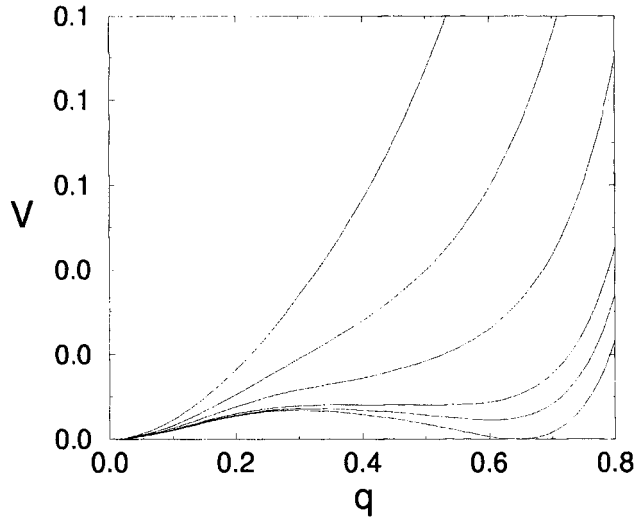

Figure 1. The effective potential $V(q)$ for the p-spin model, for several values of T. At high T, the potential is everywhere convex and, at low T, $V(q)$ exhibits two minima. Qualitatively the same behaviour is found for liquids in the hypernetted chain approximation (Franz *et al.* 1998, 1999).

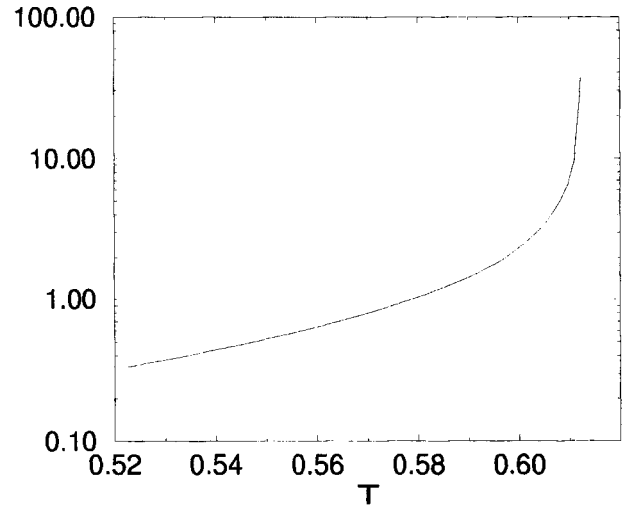

Figure 2. χ against T. The divergence of the interstate susceptibility for $T < T_c$, as calculated by Donati *et al.* (1999a,b).

While the Gibbs susceptibility remains small and regular at all temperatures, the in-state susceptibility grows and diverges as T_c is approached (Donati *et al.* 1999a,b). As suggested by the figure, the situation is similar to that of a spinodal transition, which implies $\chi \propto (T_c - T)^{-\gamma}$, with $\gamma = \frac{1}{2}$ (Donati *et al.* 1999a,b). This picture just depends on the temperature dependence of the shape of the potential, which is found to behave as described in disordered spin models (Franz and Parisi 1997, 1998, Mézard 1998), and in liquids in the hypernetted chain approximation (Franz *et al.* 1998, 1999).

By analogy with the spinodal transition, we expect that above T_c the dynamical susceptibility has a maximum as a function of time which becomes more and more pronounced and becomes displaced to higher and higher values of the time as T approaches T_c. Indeed this scenario can be verified in a dynamical framework considering the dynamics of a system which undergoes an attraction towards the initial condition (Donati *et al.* 1999a,b).

In real systems, one can expect that the results of our analysis are modified by the fact that the lifetime of the metastable states is finite and ergodicity can be recovered even below T_c. In this case two effects should be observed.

(i) The divergence at T_c should be smoothed and become a maximum.
(ii) Below T_c, because of the possibility for the system to escape from metastable states, the maximum of the susceptibility should occur at finite time.

In summary, we can interpret the growth of the dynamical correlation length found by Kob *et al.* (1997), Bennemann *et al.* (1999) and Donati *et al.* (1999a,b) in the framework of the effective potential theory of the glass transition from the analysis of random mean-field Hamiltonians. The physical picture that emerges is that close to T_c the relevant metastable states are highly correlated regions of the configuration space. The correlations between configurations in different states instead are regular and remain small for all temperatures.

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