Mesoscopic Approach to the Glass Transformation

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We propose a semimicroscopic model for the glass transformation. The long-lived nonequilibrium fluctuations are represented by quenched disorder in an equilibrium ensemble. The model predicts a sharp transition without latent heat. The liquid cannot be supercooled below the glass transition temperature, even though by adjustment of the cooling rate the glassy phase can be obtained at various temperatures. The glass is characterized by local static density fluctuations and a finite zero-frequency shear modulus.

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According to conventional thermodynamics, any liquid will crystallize if it is cooled quasistatically below the melting temperature \( T_m \). Experiments show that one can easily supercool a liquid far below \( T_m \). If crystallization by nucleation is prevented, then the metastable liquid phase becomes practically stable for timescales which are comparable to the longest experimental timescales. If that liquid is cooled further at a finite rate, it will undergo a transition—usually referred to as the glass transformation\(^1\)—into a "phase" which for most practical purposes can be viewed as an elastic solid. If a liquid is cooled sufficiently slowly that at every instant all degrees of freedom have time to equilibrate, then no glass will be formed. For the glass transformation to occur, it is essential to cool at a finite rate \( \omega_Q \), such that some fluctuations in the system cannot relax to equilibrium but are *quenched* in a high-temperature configuration. Hence the glass transformation is a *nonequilibrium* phenomenon as is manifest, for example, in the dependence of the glass transition temperature on the cooling rate.

Several attempts have been made recently to describe the glass transition either on an atomistic level,\(^2\) or with the help of kinetic theory,\(^3\) or as a purely hydrodynamic phenomenon.\(^4\) Other approaches use the concept of local orientational order in cold liquids,\(^5\) following the ideas of Frenkel.\(^8\) In this note we shall follow the latter approach.

An early analysis of the classical liquid structure by Bernal\(^9\) as well as recent computer simulations\(^10\)–\(^12\) support the original ideas of Frenkel: Cold dense liquids exhibit local orientational order with high symmetries, not necessarily those corresponding to the space-filling high symmetries allowed for crystals. Following Ref. 7, we assume that these oriented regions or "cages" can be defined in a semimicroscopic way. Indeed, computer simulations confirm\(^10\) that in the supercooled liquid these cages are very long lived and therefore a sensible building block in a theory of the liquid-glass transition. To specify the orientation of a cage we choose a set of basis vectors \( \Lambda^A(\mathbf{R}) \), for example, a tripod in three-dimensional space. In the liquid phase these tripods are uncorrelated, while in the glassy phase we expect them to be frozen in random orientations.

The stochastic freezing of the cages manifests itself in the measurable elastic properties of the glass phase. In particular the glass should exhibit a finite zero-frequency *shear modulus*. To account for these effects we consider the coupling between the local orientation of the cages \( \Lambda^A(\mathbf{R}) \) and the strain field \( \epsilon_{ab}(\mathbf{R}) = [V_{a,b}(\mathbf{R}) + V_{b,a}(\mathbf{R})]/2 \). Here \( u_b(\mathbf{R}) \) denotes the instantaneous displacement of the cage from its average position.

As discussed above the glass transformation is a non-equilibrium phenomenon. Hence a theoretical approach should start from the equations of motion for fluctuations on all time scales including \( 1/\omega_Q \). In practice the cooling rates can be extremely small (\( \omega_Q \sim 10^{-2} \text{ s}^{-1} \) for good glass formers). We suggest that for time scales \( < \omega_Q^{-1} \) an equilibrium statistical mechanics description may be adequate, provided the existence of quenched fluctuations is taken into account. We treat the orientational fluctuations as well as small displacements of the cages as thermal degrees of freedom, whereas the average positions of the cages are considered fixed and therefore belong to the class of quenched fluctuations. This implies that the diffusion of cages is suppressed on time scales \( < 1/\omega_Q \).

Following Ref. 7 we consider a free-energy functional
which consists of three parts:


The orientation of the tripods is a continuous variable. However, the symmetry of the cages induces a local anisotropy, which favors discrete orientations. To simplify the mathematics we represent these preferred orientations by p-state Potts variables \( \Lambda^q(i) = S^q(i) = \delta_{S(i),q} - 1/p \) with \( q = 1,2,\ldots,p \). This approximation is believed to capture the essential features of the problem—at least in mean-field theory.\(^{6,13}\) We do not want to specify the local symmetry any further and leave the dimension \( p \) of the Potts variable arbitrary.

We postulate the interaction between the cages to be of the form

\[ F_S[S] = \sum_{ij} \sum_{pq} J_{ij}^p S^p(i) S^q(j) . \]  

The orientational degrees of freedom generate a local stress field

\[ \sigma_{ab}^{\text{int}}(i) = \sum_{pq} G_{ab}^{pq}(i,j) S^p(i) S^q(j) , \]

that couples linearly to the elastic strain:

\[ F_E[S,e] = \sum_i \text{Tr}[e(i) \sigma_{ab}^{\text{int}}(i)] , \]

where \( \text{Tr} \) refers to the Cartesian indices. The elastic free energy for small displacements of the cages is given by

\[ F_E[e] = \frac{1}{2} \sum_i \text{Tr}[e(i) C e(i)] . \]

Here \( C_{abcd} = \lambda \delta_{ab} \delta_{cd} + \mu \delta_{ac} \delta_{bd} + \delta_{ad} \delta_{bc} \) are the bare elastic coefficients, which in general are different from the measured elastic coefficients. In particular one might consider the possibility of a vanishing bare shear modulus, \( \mu = 0 \), as will be discussed below.

Following ideas which have been proposed for spin glasses\(^{14}\) and orientational glasses,\(^{13,15-17}\) we introduce quenched fluctuations into our model: We assume that the local stress tensor as well as the direct interaction between the tripods have fluctuating contributions. In the supercooled liquid close to the glass transition, we treat these fluctuations as quenched random variables. For simplicity we choose \( G_{ab}^{pq} = \delta_{pq} G_{ab} + \delta_{ab} G_{pq} \) and \( J_{ij}^p = \delta_{ij} (J + \delta J) \), and consider Gaussian fluctuations only,

\[ \langle \delta G_{ab}(i,j) \delta G_{cd}(i,j) \rangle = K_{ij} G_{abcd} , \]

\[ \langle \delta J(i,j) \delta J(i,j) \rangle = K_{ij} J , \]

where square brackets denote configurational average. Here \( K_{ij} \) is a nonrandom function of the separation \( i \sim j \). The variance of the quenched variables is a measure for the amount of disorder in the system and therefore increases with the cooling rate. Equations (1)-(5) define the model completely. It is a generalization of various models which have been studied previously.\(^{7,13,17}\)

We concentrate here on that part of the phase dia-

gram where the systematic parts of the tripod interaction and of the local stress are small, so that there is no long-range orientational order. In this case it does not matter whether the fluctuations of the Potts coupling are chosen isotropic as above or anisotropic in general. The anisotropy is, however, important if one wants to consider a phase with long-range orientational order. In that case the anisotropy mixes longitudinal and transverse components, whose freezing occurs simultaneously.

The random Potts model without the coupling to the elastic strain has been analyzed by Eldridge and Sherrington\(^{17}\) and Gross, Kanter, and Sompolinsky.\(^{13}\) They find a transition from the disordered paramagnetic phase to a Potts-glass phase at \( T_g^2 = J \). The glassy phase is characterized by a nonzero value of the Edwards-Anderson order parameter \( g \),

\[ Q_m = \langle \rho(\delta S(i),j) \rangle - 1 \frac{1}{p} \]

\[ = p(\rho(\delta S(i),j) - 1) \]

\[ = q(p \delta_{\rho x} - 1) \]

whereas the average magnetization vanishes, \( m = \langle \rho(\delta S(i),j) \rangle = 0 \). Here and in the following angular brackets denote the thermal average and square brackets the configurational average. The order of the glass transition depends on the dimensionality \( p \) of the Potts variable. For \( p < 4 \) the transition is continuous, whereas for \( p > 4 \) it is a first-order transition. In either case, though, there is no latent heat.\(^{13}\) The specific heat is discontinuous at \( T_g \) for \( p > 4 \) and has a cusp at \( T_g \) for \( p < 4 \).

These results were derived in the mean-field approximation, \( K_{ij} = 1/N \), with use of the replica technique to average over the quenched disorder. In the glassy phase, replica symmetry is broken by the appearance of many ergodic components. Their mutual overlap is described by a monotonic function \( q(x) \) with \( 0 \leq x \leq 1 \).

We now discuss the main results of our model [Eqs. (1)-(5)], which have been obtained in mean-field approximation with use of the replica technique.

(1) The elastic degrees of freedom do not destroy the freezing transition of the Potts variables, provided the coupling is weak. Hence the Potts glass transition can be identified with the liquid-glass transformation.

(2) The glass transition temperature \( T_g^2 = J + \frac{1}{4} \times \text{Tr}(GC^{-1})^2 \) is proportional to the variance of the quenched disorder. We assume the weak-coupling limit defined by \( \text{Tr}(GC^{-1}) < \sqrt{J} \). When we recall that the variance is a measure of the quench rate, this finding is in agreement with the experimentally known dependence of \( T_g \) on the rate of quench.\(^{1}\)

(3) The absence of a latent heat—indepedent of the order of the transition—is in agreement with experiments on the glass transformation.\(^{1}\)

(4) The liquid state does not exist as a metastable state in the glassy phase, as shown by Gross, Kanter, and Sompolinsky.\(^{13}\) Hence one cannot supercool a liquid below the glass transition temperature, even though by
adjusting the rate of cooling one can obtain the glassy phase at various temperatures.

So far we have only discussed the thermodynamic properties of the liquid-glass transition. The mutual correlations of the tripods are not directly accessible to experiment. Since the local cages do not correspond to microscopic degrees of freedom, it is not obvious how to measure the frozen orientational order. It is therefore very important that the orientational degrees of freedom are coupled to the remaining degrees of freedom in the system: The tripods generate a local fluctuating stress that couples to the elastic strain. Thus the measurement of various stress-tensor correlation functions gives us an indirect access to the correlations of the tripods. The primary criterion for the glass transformation is the development of shear elasticity. Hence we restrict ourselves here to an analysis of the change in the elastic constants due to the stochastic freezing of the tripods. The main conclusions are these:

(5) There is no macroscopic volume change at the glass transition. The glassy phase is characterized by local static density fluctuations \( \langle \Delta \rho (r) \rangle \neq 0 \), while on the average \( \langle \Delta \rho (r) \rangle = 0 \).

(6) The elastic compliance \( S \equiv [\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2] = C^{-1} \) is reduced in the glassy phase. In the weak-coupling limit we find

\[
\bar{C}_{abcd} = C_{abcd} + \beta (p - 1) G_{abcd} \int_0^1 q^2(x) dx. \tag{7}
\]

Now let us assume that the bare elastic properties of the liquid are characterized by a vanishing shear modulus but a finite bulk modulus \( K \); i.e., \( C_{abcd} = K \delta_{ab} \delta_{cd} \). Then freezing of the orientational degrees of freedom generates a finite shear modulus

\[
\mu = \beta (p - 1) G_{1212} \int_0^1 q^2(x) dx. \tag{8}
\]

The change in the elastic constants is continuous, independent of the order of the transition. Experimentally one observes a sharp increase in the low-frequency elastic constants. When comparing our results to experiment, one should keep in mind that in a real system, the quench rate is small but finite. Our analysis only applies to the response at frequencies which are larger than the quench rate. At small but finite frequencies the shear modulus of the supercooled liquid is not strictly zero, but small as compared to its value in the glassy phase.

We briefly outline how these results were obtained. To perform the average over the quenched disorder, we consider the partition function function \( Z^n \) of \( n \) replicas of the original system:

\[
Z^n = \int \prod d \epsilon_{ab} (i) \frac{\text{Tr}[\epsilon_{ab} (i)]}{\langle \epsilon_{ab} (i) \rangle} e^{-\beta H}, \tag{9}
\]

\[
H = \frac{1}{2} \sum_{i,a} \text{Tr}[\epsilon_{a} (i) C \epsilon_{a} (i)] - \sum_{i,a} \text{Tr}[\epsilon_{a} (i) \sigma_{a}^{\text{int}} (i)] - \sum_{a,p,q} \beta \int_0^1 S_a^p (i) S_a^q (j). \tag{10}
\]

Here \( a \) labels the replica and the parameters of the interaction have been chosen such that no long-range orientational order exists. The elastic compliance \( S = \langle 1/T \rangle [\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2] = \langle \bar{C} \rangle^{-1} \) is given by the strain-strain correlation function. We introduce a new field \( \bar{\epsilon}_{a} (i) = \epsilon_{a} (i) + C^{-1} \sigma_{a}^{\text{int}} (i) \) and calculate

\[
\langle \epsilon_{a} (i) \epsilon_{b} (j) \rangle = \langle \bar{\epsilon}_{a} (i) \bar{\epsilon}_{b} (j) \rangle + \langle C^{-1} \sigma_{a}^{\text{int}} (i) C^{-1} \sigma_{b}^{\text{int}} (i) \rangle
\]

\[
= TC^{-1} \delta_{ab} + \sum_{p,j} C^{-1} \delta G(i,j) C^{-1} \delta G(i,l) \langle S_a^p (i) S_a^q (j) S_a^p (j) S_a^q (l) \rangle. \tag{11}
\]

To obtain the last equality we have used the explicit form of \( \sigma^{\text{int}} (i) = \sum_{p,j} \delta G(i,j) S_a^p (i) S_a^q (j) \). Equation \( 11 \) gives the change in the elastic constants due to the coupling to the orientational degrees of freedom. The expression of Eq. \( 11 \) is an exact result for our model. To make further progress we have to resort to approximations; namely, we shall assume that the fluctuating internal stress \( \delta G \) is small. Then the configurational average of the strain-strain correlation is approximately given by

\[
\langle \epsilon_{a} (i) \epsilon_{b} (i) \rangle = TC^{-1} \delta_{ab} + C^{-2} G \int_0^1 \frac{1}{N \sum_{j,p,q} \langle S_a^p (i) S_a^q (j) S_a^p (j) S_a^q (l) \rangle} \tag{12}
\]

The four-spin correlation represents four variable correlations of the orientational degrees of freedom and has to be evaluated for the pure Potts model (without coupling to the elastic degrees of freedom). For \( a = \beta \), the four-spin correlation is given by

\[
\frac{1}{N} \sum_{j,p,q} \langle S_a^p (i) S_a^q (j) S_a^p (j) S_a^q (l) \rangle = (p - 1) + p(p + 2) \frac{1}{N} \sum_{j,p} \langle S_a^p (i) S_a^q (j) \rangle. \tag{13}
\]
The first term renormalizes the bare elastic constants independent of the state of the tripods. It will be absorbed into the definition of the bare elastic constants. The second term does not contribute, as long as there is no long-range orientational order, as we assume here. For $\alpha \neq \beta$ the four-spin correlation can be factorized in mean-field theory. If we use that in the replica theory,

$$
\langle \langle e^2 \rangle \rangle = \lim_{n \to 0} \frac{1}{n(n-1)} \sum_{\alpha \neq \beta} \langle e_{\alpha} e_{\beta} \rangle,
$$

we obtain the result of Eq. (7).

Note that the four-spin correlation in Eq. (11) is not the uniform order-parameter susceptibility. If we consider a short-range model, i.e., $G(i,j)$ nonzero for a few nearest neighbors only, then all distances in the four-spin correlation are restricted to be small.

The model under discussion is certainly oversimplified. However, it already accounts for some of the salient features of the glass transition and the glassy state. It would be most interesting to study the dynamics of the model in order to see whether it can explain the viscoelastic anomalies near the glass transition. Another possible application of the model is in the field of plastic solids. In these substances local orientational degrees of freedom correspond to actual microscopic degrees of freedom, which do affect the properties of the host lattice.

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