Nucleation model for the description of glass formation

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We present in this letter a model of glass formation using energy barriers and a crystal nucleation process. We then analyze the corresponding dynamical equation in the vicinity of the stationary solutions. The occurrence of a pure amorphous solution (i.e. glass) is due to the contribution of a ratio λ depending on the cooling rate and the crystal nucleation frequency. We also construct time-temperature transformation (T-T-T) curves in order to relate the model with the kinetic treatment of glass formation.

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The formation of glasses requires cooling to a sufficiently low temperature, below the glass transition temperature, without the occurrence of detectable crystallization.

One of the most comprehensive theory of dynamical processes in glasses is the so-called mode-coupling theory (MCT), developed by Goetze and others [1]. The MCT is based on a set of non-linear damped second-order differential equations, which couple the density correlation functions of a supercooled liquid in a retarded way. These equations have several interesting properties, such as the possibility of a stretched-exponential time decay for the correlation function for particular values of the strength of the non-linear coupling. They exhibit, also, a kind of "ideal glass" transition, at an ideal glass temperature $T_C$, corresponding to a singularity of the equations. Nevertheless, the major limitation is that, so far, only spherically symmetric interatomic interactions have been considered, as for instance the computer calculation by Bengtzelius on a Lennard-Jones system [2]. Thus, the complexities in real glass-forming systems arising from covalent interactions (e.g. silica) are neglected, so that the theory seems only well-adapted for fragile glass-forming liquids (e.g. organic or molecular glasses). There have been recently also theoretical developments of mean-field models in order to understand the role of different factors in the glass transition, such as configurational entropy [3], energy barriers [4] or free energy [5], some of them being inspired from spin glass models. However, the critical question in discussing glass formation is not whether the solid will be obtained from a melt quench, but how fast a given liquid must be cooled in order to prevent the kinetic processes involved in crystallization. Thus, the cooling rate and the crystal nucleation rate should play the major role.

The work presented here consists in the construction of an exactly solvable mean-field model of crystalline nucleation, based on a probabilistic description, which can be described by a dynamical equation. Although this model is rather abstract and has no thermodynamic transition, we believe that it captures at least parts of the physics involved in the glass transition and explains it in a simple fashion. The model attempts also to relate factors that are widely viewed as decisive in the formation and preparation of glasses, namely structural, kinetic and thermodynamic factors [6]. We shall see that the probability of occurrence of an amorphous phase (identified with a supercooled liquid below the melting temperature and then with a glass when temperature has decreased enough) depends strongly on the cooling rate. Let us try to describe what happens on a microscopic scale when a liquid is cooled and translate this in terms of thermodynamics.

A liquid at high temperature (with $T$ higher than the melting temperature) should contain a lot of aggregates of different sizes and shapes. The atoms which compose some of the aggregates may be already organized with periodic character (identified with a crystalline nucleus), whereas others do not exhibit this feature and may display a disordered structural organization (amorphous structure).

Construction of the model. Let $p_c = p(C_0)$ be the probability of finding an atom, in a crystalline aggregate, being in the initial liquid configuration $C_0$. The structure associated with this aggregate is size-independent and there is no reference to a spatial structure, therefore the model is of mean-field type. In this description, the probability $p_c$ corresponds to the number of atoms which are already trapped inside a crystalline unit cell or a set of such cells, over the total number of atoms. Similarly, we define the probability of finding an atom inside an amorphous aggregate by $1 - p_c$. The glassy state will thus correspond to $p_c = 0$ at low temperature and the crystal to $p_c = 1$. The probability $p_c$ depends at least on time, temperature and the cooling rate. When the temperature is decreasing, the aggregates start to grow by nucleation. The energy barriers related to such agglomeration processes depend, of course, on the nature of the clusters which are involved. Therefore, we define for a crystal-crystal nucleation an energy barrier of $2E_c$, for a crystal-amorphous structure agglomeration an en-
energy barrier of $E_c + E_a$ and for an amorphous-amorphous structure agglomeration $2E_a$. $E_c$ is the mean energy stored in a crystalline cluster and $E_a$ the one stored in an amorphous structure. This means that the initial configuration $C_0$ can be considered as a system with two energy states $E_c$ and $E_a$ and that the atoms can be treated as particles able to occupy one of these states. After agglomeration or nucleation, the system is in a final configuration $C$. It is composed of three energy states ($2E_c$, $E_a + E_c$ and $2E_a$), and the repartition of the particles can be computed. The probability of finding an atom trapped in such a new state may be proportional to the product of the initial probabilities (i.e. to the number of related particles) and a Boltzmann weight, inspired from the Thouless-Anderson-Palmer (TAP) description \(^7\) of spin glass theory (e.g. the pure crystal state with probability $p_{cc}$ is proportional to $p_c^2$). Such a description has been also used in a growth model of polygons \(^8\) and in structural glass models \(^9\).

$$p_{ij} = \frac{(2 - \delta_{ij})}{Z}(1 - p_c)^{\delta_{ia} + \delta_{ja}} p_c^{\delta_{jc} + \delta_{kc}} e^{-\alpha(\delta_{ic} + \delta_{jc})}$$

where $\alpha = \beta(E_c - E_a)$ with $\beta$ the reverse temperature. Since the probabilities are all normalized by the factor $Z$, only the difference $\alpha$ is relevant. The normalizing factor $Z$, which can be regarded as a TAP-like partition sum ensures that $\sum_{i,j} p_{ij} = 1$, as it should be. During nucleation, an atom trapped inside a crystalline state, can be found in the nucleated configuration $C$ (energy states $2E_c$ or $E_a + E_c$) or still in the initial configuration $C_0$ (energy state $E_a$). Its probability is expressed by:

$$p_c(t) = \left[1 - s(t)\right] p(C_0) + s(t) \ p(C)$$

where:

$$p(C) = \frac{1}{2} \left[ 2 \ p_{cc} + p_{ac} \right]$$

The function $s(t)$ with $0 \leq s(t) \leq 1$, introduced above depends on time and represents the growth rate (i.e. a measure of the number of nucleated crystalline aggregates which are already formed). Its derivative $\dot{s}(t) = ds/dt$ is then the nucleation frequency or growth speed. When $s(t) = 1$, the nucleation process is finished.

The derivative of the probability $p_c(t)$ obeys the following dynamical equation, which is constructed from the equations above and which takes into account the effect of the cooling rate $Q = -dT/dt$.

$$\frac{dp_c(t)}{dt} = \dot{s}(t) \left[ p(C) - p(C_0) \right] - Q \frac{\partial p(C)}{\partial T}$$

At finite temperature and for long enough times, the model reaches a stationary state, corresponding to thermal equilibrium, thus we shall be interested in the stationary solutions of the dynamical equation. We can solve this equation in terms of the probability $p(C_0)$, since the probability $p(C)$ of the final state is also constructed with them. This should happen in the liquid and supercooled state for very slow cooling rates and in the final solid for $T \simeq 0$. Obvious solutions of the equation are $p(C_0) = 0$ (pure amorphous state) and $p(C_0) = 1$ (pure crystal state). Besides solutions without physical meaning ($p(C_0) > 1$), an intermediate solution exists which shifts with the cooling rate $Q$, the crystal nucleation frequency $\dot{s}(t)$ and the temperature:

$$p_c^{int} = \frac{e^u \left[ 2 - \frac{\alpha}{\beta} u + \frac{\alpha}{2\beta} u \coth u \right]}{4 \sinh u}$$

where $\Lambda = Q/\dot{s}(t)$ and $u = \alpha/2$. The existence of this intermediate solution depends on $\Lambda$, which must be inside region II of fig. 1.

**Dynamics of crystal and glass formation.** In order to see in which direction and under what condition the system can evolve, we have performed the linearization of the dynamical equation in the vicinity of the stationary solutions and computed the corresponding relaxation times $\tau_0(T)$ and $\tau_1(T)$, which characterize the convergence of the nucleation process towards equilibrium. The behavior of the liquid is mainly driven by the factor $\Lambda$ and typical situations occur, according the sign of $\alpha$.

![FIG. 1. A plot of the critical factors $|\Lambda_2|$ (solid line), which yields $p_c^{int} = 1$, and $|\Lambda_2|$ (dashed line), which yields $p_c^{int} = 0$, as a function of temperature $T$ with $E_c - E_a = -1$. The intermediate solution $p_c^{int}$ exists only if $|\Lambda_1| < |\Lambda| < |\Lambda_2|$.](image-url)
When \( \alpha < 0 \) (the crystalline energy barrier being lower than the amorphous one), there are only two solutions and the \( p(C_0) = 1 \) one is an attractor. This means that every fluctuation \( \xi \) in the probability which could occur during the nucleation process, tends to vanish with increasing time. The dynamical equation becomes: \( \tau_1(T)d\xi = -\xi dt \) with relaxation time:

\[
\tau_1(T) = \frac{\tanh \frac{2}{T} - 1}{(\frac{2\alpha}{T^2} + 4) \tanh \frac{2}{T} + \frac{2\alpha}{T}}
\]

Growth is then made only out of atoms being part of crystalline aggregates. On the contrary, it is easy to verify that a fluctuation \( \eta \) in the vicinity of the amorphous solution \( p(C_0) = 0 \) will grow exponentially with increasing time and the relaxation time \( \tau_0(T) \) \( \tau_0(T) d\eta = \eta dt \):

\[
\tau_0(T) = -\frac{1 + \tanh \frac{\eta}{T}}{(\frac{2\alpha}{T^2} - 4) \tanh \frac{\eta}{T} - \frac{2\alpha}{T}}
\]

So, there is no dissipation of an amorphous fluctuation \( \eta \). We believe that this situation is typical of systems for which there is no possibility in glass formation (e.g. all the elements except selenium, sulfur and tellurium).

An interesting feature of this dynamical analysis is given by the relaxation times \( \tau_0(T) \) and \( \tau_1(T) \) which exhibit a very different behavior following the process (cooling or heating). We define by \( \tau_{equ} \) the relaxation time of a process at thermal equilibrium (i.e. when \( \Lambda \) is negligible, so \( 1/\tau_{equ} = 1 - e^{\alpha} \). For low temperatures \( (T \to 0) \), the dynamics of the process is close to equilibrium since \( \tau_1(T) \approx \tau_{equ} \). Starting from a high \( T \) liquid, one observes that \( \tau_1 \) decreases when temperature goes down. This means that it becomes more and more easier for the system to fall on the crystalline attractor. \( \tau_1 \) exhibits a minimum at a certain value \( T^* = -\Lambda + \sqrt{\Lambda^2 - \Lambda(E_c - E_a)} \), which we identify with the melting temperature. It is the temperature at which the driving force towards the crystalline aggregation \( (p(C_0) = 1) \) is at its maximum. In the heating process \( (\Lambda < 0) \), the \( p(C_0) = 0 \) and \( p(C_0) = 1 \) solutions are both attractive, the latter with a relaxation time \( \tau_1 \approx \tau_{equ} \) for low \( T \), but this solution diverges rapidly in the vicinity of a temperature \( T_1 \) close to \( T^* \). For \( T > T_1 \), the crystal solution is unstable and the amorphous (liquid) solution only is attractive. In the range \( 0 < T < T_1 \), the intermediate solution exists but it is unstable. The described dynamical behavior shows that a crystalline solid which is heated from a low temperature, remains the preferential structure up to a temperature \( T_1 \) close to the temperature \( T^* \). There, the crystal relaxation time \( \tau_1 \) diverges, which allows the possibility for the system to investigate other possible structural pathways, such as the amorphous one.

When \( \alpha > 0 \), there is a possibility of formation of an amorphous solid, because the \( p(C_0) = 0 \) solution is attractive, whereas, the crystalline state is repulsive. In this situation, \( \tau_0(T) \) displays the following behavior: starting from a high \( T \) liquid phase, one can easily check that the fluctuations in the vicinity of the crystalline solution grow exponentially with a relaxation time \( \tau_1(T) \). The \( \tau_0(T) \) relaxation time is negative and close to 0. It starts to decrease when the temperature decreases (fig. 2, circles, i.e. the dynamics of the attractor becomes slower. The liquid state is still the preferential one, but the time needed for a created fluctuation to vanish, increases dramatically. At some temperature \( T(\Lambda) \), related to the factor \( \Lambda \), we have \( \tau_0(T) \to -\infty \). We identify this temperature with the glass transition temperature \( T_g \), which depends on the cooling rate, as it should do. The configurational change \( \gamma \) which may cause the relaxation for the low-temperature supercooled liquid has become infinitely slow, thus the liquid behaves as a solid, and \( T_g \) satisfies:

\[
\tanh \left[ \frac{E_c - E_a}{2T_g} \right] = \frac{\Lambda(E_c - E_a)}{4T_g^2 - \Lambda(E_c - E_a)}
\]

On the contrary, we can remark that starting from \( T = 0 \) (at equilibrium) \( \tau_0(T) \) is close to \( \tau_{equ} \) and the \( p(C_0) = 0 \) solution is now repulsive (fig. 2, solid line with circles). \( \tau_0(T) \) rapidly falls to 0, so the configurational change is possible and crystalline fluctuations can grow easily, in agreement with current observation stating that recrystallisation occurs when a glass is heated up.
Construction of the time-temperature-transformation (T-T-T) curves. As we have constructed this model by using a simple crystallization process, it is interesting to relate it to results concerning the kinetic treatment of glass formation, which describe the crystallization process by considering both nucleation and crystal growth and estimate the cooling rates required to form glasses. Thus, kinetic treatments of glass formation are based on identifying a certain value of the volume fraction crystallized \( v_c/v \), as borderline between an amorphous and a crystalline solid \([10]\) \((v_c/v)\) is generally of the order of the experimentally just detectable degree of crystallinity, i.e. around \(10^{-6}\)). The results of such investigations are plotted on a \( T-T \) plane for different values of \( v_c/v \) and represent the time-temperature-transformation (T-T-T) curves \([6]\).

![Figure 3](image_url)

**FIG. 3.** The T-T-T curves for different \( s(t) \) behavior a) \( s(t) = 1 - e^{-t} \). Solid line (with points) \( T_0 = 1.4 \), solid line \( T_0 = 1.7 \), both with a fraction of \( x_c = 10^{-6} \). Dashed line: \( T_0 = 1.7 \) and \( x_c = 0.2 \). b) \( s(t) = t \). Dots: system with \( T_0 = 1.7 \), \( x_c = 10^{-6} \). As before, \( E_c - E_{\alpha} = -1 \) for all situations.

In our mean-field description, the extensive variables \( p_c \) and \( v_c \) are related by: \( v_c = p_c v \), where \( v \) is the total volume of the system. Therefore, if \( v_c = p_c v \) is maintained constant, the right hand side of the dynamical equation will be equal to 0 for any temperature. We can then compute the T-dependence of the factor \( \Lambda \) and obtain after integration a \( T-t \) relationship. If \( x_c \) is the fraction of crystalline atoms (with probability \( p_c^{\text{nat}} \)), then \( \Lambda \) must satisfy:

\[
x_c(e^\alpha - 1)^2 - e^{2\alpha} + e^\alpha = -\frac{\Lambda}{T} \alpha e^\alpha = -\frac{\alpha}{T} \frac{dT}{s(t)dt}
\]

and integration yields:

\[
\alpha \left( \frac{T}{T_0} - 1 \right) + \ln \left[ \frac{\alpha(x_c - 1) - x_c}{\alpha_0(x_c - 1) - x_c} \right] = s(t)
\]

where \( T_0 \) is the initial temperature of the melt and \( \alpha_0 \) the corresponding factor \( \alpha \). We have plotted different situations in fig. 3 for different \( t \)-dependences of the function \( s(t) \). One natural (and the simplest) dependence for \( s(t) \) is the exponential one with \( s(0) = 0 \) and \( s(\infty) = 1 \), in order to agree with the construction of \( p_c(t) \). Figure 3 shows the dependence of the temperature with time if one keeps \( x_c \) constant during nucleation. The curves displayed show the same behavior as the constructed T-T-T curves by Uhlmann \([3,10]\). i) The T-t curve with a lower degree of crystallinity \((x_c = 10^{-6})\) envelopes the curve with a higher degree \((x_c = 0.2)\), i.e. the temperature must decrease more rapidly, as seen on the figure. ii) The effect of the initial temperature \( T_0 \) can also be observed.

In conclusion, we should stress that the dynamical analysis presented here puts forward the general accepted picture that a glass is obtained by cooling a melt enough in order to avoid nucleation, although this picture displays no transition in the thermodynamical sense. However, different physical parameters are involved in this very complex transition such as free energy, cooling rate, nucleation frequency, initial temperature or structure. The work presented here was an attempt for the description of the glass formation using a nucleation process. Forthcoming work will include structural factors \([11]\).

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