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Review

Relaxation dynamics near the sol–gel transition: From cluster approach to mode-coupling theory

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Abstract. A long standing problem in glassy dynamics is the geometrical interpretation of clusters and the role they play in the observed scaling laws. In this context, the mode-coupling theory (MCT) of type-A transition and the sol–gel transition are both characterized by a structural arrest to a disordered state in which the long-time limit of the correlator continuously approaches zero at the transition point. In this paper, we describe a cluster approach to the sol-gel transition and explore its predictions, including universal scaling laws and a new stretched relaxation regime close to criticality. We show that while MCT consistently describes gelation at mean-field level, the percolation approach elucidates the geometrical character underlying MCT scaling laws.

1 Introduction

A large variety of soft matter systems undergoes a transition from a fluid to a solid-like state when one of the parameters controlling the system state (temperature, volume fraction, etc.) is changed. Such transition is accompanied by a rapid growth of the relaxation time, often without any apparent increase of long-range spatial correlations. Consequently, the system is structurally disordered while its dynamics appears arrested on the experimental timescales. Paradigmatic examples include, but are not limited to, structural glasses [1,2], gels [3–5], colloids [6] and granular matter.

Since the linear size of elementary units in these materials spans several orders of magnitude (from nm in simple liquids to μm in colloids and mm in granular media) and the possible very different nature of their interactions, one can naturally wonder whether the slow relaxation observed near this transition, and the resulting amorphous state, may exhibit features which are universal in the sense of statistical

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mechanics, i.e., features which do not depend on the microscopic details of the system under consideration and their specific interactions.

The first conceptual problem one has to deal with when addressing such an issue is whether the amorphous state is the result of a genuine thermodynamic phase transition or rather a purely dynamic effect in which there is no true static ergodicity breaking. Secondly, one would like to have a geometric characterization of slow relaxation, e.g., in terms of suitably defined clusters, and, more generally, one would like to identify the appropriate order parameter describing the phase, where ergodicity is broken. For generic amorphous systems, these two difficulties turn out to be challenging even at mean field theory level which is, in statistical mechanics, the very preliminary step for understanding universal scaling features.

We focus here on the slow relaxation dynamics near the sol-gel transition. From a theoretical point of view, gelation naturally lends itself to a cluster approach in which universal glassy features are obtained in terms of percolation scaling exponents. Therefore, it may arguably represent the first crucial step towards the understanding of more complex situations (e.g. structural glasses) in which there is no obvious description in terms of clusters.

The present contribution is organized as follows. After a preliminary discussion of the nature of the sol-gel transition (Sect. 2) we present a percolation-based cluster approach to the relaxation dynamics near the gelation point (Sect. 3). Then, we discuss the mode-coupling theory of continuous glass transitions (Sect. 4). The link between these two distinct and independent theoretical settings is suggested in the Sect. 5. Finally, in the conclusions, we present some open problems and speculations about the nature of weak and strong gels.

2 Gelation: Static or dynamic transition?

Gelation corresponds to the transformation of a viscous liquid (sol) into an elastic amorphous solid (gel). This process generally arises from the bonding of multifunctional monomers in solution and leads, above a certain monomer concentration threshold, to the formation of a macroscopic polymer network which enables the system to bear mechanical stresses. For an interesting kinetic model for gelation see Ref. [7]. From a geometric point of view, the sol-gel transition is the manifestation of the formation of a percolating cluster of crosslinked polymers which has a fractal structure [3,4,8]. This view has been supported by several experiments (for a review see [5] and references therein).

The gel properties generally depend on the nature of the reaction involved in the bonding formation. *Chemical* gels are characterized by covalent bonds which are irreversible and permanent: once the gel is formed there is no way to go back to the original state we started with. Boiled eggs and dental filling pastes are some common examples of chemical gels in which polymerization is driven by temperature and light, respectively. *Physical gels* (such as gelatins), instead, features reversible bonds (e.g. hydrogen bonds) which break and form continuously at a fixed rate controlled by thermal fluctuations. Depending on the bond lifetime, which can vary from μs to s, physical gels can be classified in *weak* or *strong*. In strong gels, clusters keep their identity and never break on the experimental time-scale, so they share similar features with chemical gels.

At experimental level [9–11], it is generally known that the sol-gel transition always occurs continuously and is typically associated with the onset of non-exponential, *stretched* relaxation behavior and a dramatic increase of the relaxation time or viscosity, a peculiar distinctive feature of glassy dynamics [12].

At theoretical level, percolation theory is the most natural approach for describing the scaling features associated with the spanning polymer network, as early suggested by Flory [13] and Stockmayer [14]. They consistently predict that the sol-gel transition has a continuous nature, as experimentally observed. An important issue largely debated (see [15] and references therein) is whether the underlying free-energy of the system is regular and therefore the slow relaxation near the gelation point should have a purely dynamical origin. It has been suggested [16] that while chemical gels exhibit a singularity in the free energy, resembling in part spin glasses or the random field Ising model [17], physical gels have a purely dynamical origin. We postpone the discussion of this point to the final part of this contribution and focus now on the percolation description of the slow dynamic near the sol-gel transition.

3 Dynamic cluster approach to sol-gel transition

The static percolation approach used to describe the structural properties of gelation can be extended to deal with the dynamic relaxation near the sol-gel transition. Here we discuss a cluster approach [18] originally developed in Ref. [19] that allows to describe the scaling features of relaxation in terms of percolation critical exponents and one additional dynamical exponent. For the sake of comparison with mode-coupling theory, we particularize the results obtained in Ref. [19] to the mean-field case (corresponding to a system with infinite spatial dimensionality).

We consider a system of randomly distributed monomers with a fixed volume fraction ϕ. At $t = 0$, permanent bonds are introduced at random between monomers located within a distance chosen to represent the range of monomers interaction [20]. Following the percolation approach [3,4], the sol-gel transition is defined as the point corresponding to the formation of an incipient spanning cluster. Accordingly, the results of percolation theory [8] imply that in the sol phase, near the threshold, the cluster size distribution $n(s)$ is

$$n(s) \sim s^{-\tau} \exp\left(-\frac{s}{s^*}\right), \tag{1}$$

where τ is the Fisher exponent, s^* is a cut-off value proportional to ξ^{d_f}, d_f is the fractal dimension, and ξ is the connectedness length, which diverges at the threshold with the exponent ν. In the gel phase, there is a finite density P_∞ of particles in the percolating cluster and, in agreement with the results of percolation theory [8], the distribution of finite-size clusters is given by

$$n(s) \sim s^{-\tau} \exp\left[-\left(\frac{s}{s^*}\right)^{(d-1)/d}\right], \tag{2}$$

which coincides with Eq. (1) in the mean-field limit, where the system dimension $d \to \infty$. We can then assume that the cluster structure evolves in time as follows.

- Every cluster decays exponentially in time,

$$f_s(t) \sim \exp\left(-\frac{t}{t_s}\right)\cdot \tag{3}$$

- The lifetime of any cluster increases with its size as [24]:

$$t_s \sim s^x, \tag{4}$$

  where the exponent x depends on the microscopic mechanism responsible for the single cluster relaxation.

Using the above assumptions, which are borne out by experiments and numerical simulations, and neglecting the correlation between particles belonging to different clusters, one can compute several dynamical quantities such as the self-intermediate scattering function, the dynamical susceptibility, the Van–Hove function, and the non-Gaussian parameter [19]. Here we are interested in the time correlation function, $\Phi(t)$, which is defined as

$$\Phi(t) = \sum_s s\, n(s)\, f_s(t). \tag{5}$$

Replacing the sum in the above equation by an integral, with some approximations (for details see Ref. [19]), the time dependence of $\Phi(t)$, is expressed in terms of the critical percolation exponents β and τ, along with the dynamic exponent x. The predictions are:

(i) At the gelation threshold, $\phi = \phi_c$, $\Phi(t)$ is a power-law:

$$\Phi(t) \sim t^{-a}, \tag{6}$$

where

$$a = \frac{\tau - 2}{x}\cdot \tag{7}$$

(ii) In the sol phase, $\phi < \phi_c$, at a distance $\epsilon = (\phi_c - \phi)/\phi_c$ from the threshold, the long time limit ($t \geq \tau_\epsilon$) relaxation is described by a combination of algebraic and stretched exponential decays:

$$\Phi(t) \sim |\epsilon|^\beta \left(\frac{\tau_\epsilon}{t}\right)^c \exp\left[-\left(\frac{t}{\tau_\epsilon}\right)^y\right], \tag{8}$$

with

$$y = \frac{1}{x+1}, \qquad c = y\left(\tau - \frac{3}{2}\right)\cdot \tag{9}$$

This form agrees with experimental [9–11] and numerical findings [25,26] in gelling systems.

(iii) In the gel phase, $\phi > \phi_c$, at distance $\epsilon = (\phi_c - \phi)/\phi_c$ from the threshold, one obtains exactly the same form for the relaxation function, once the long-time limit has been subtracted

$$\Phi(t) - P_\infty \sim |\epsilon|^\beta \left(\frac{\tau_\epsilon}{t}\right)^{c'} \exp\left[-\left(\frac{t}{\tau_\epsilon}\right)^{y'}\right]\cdot \tag{10}$$

where P_∞ is the density of the percolating cluster, which goes to zero at the threshold as $P_\infty \sim |\epsilon|^\beta$, and the exponents y' and c' are given by

$$y' = \frac{1 - \frac{1}{d}}{1 - \frac{1}{d} + x}, \qquad c' = y' \frac{\tau - \frac{3}{2} - \frac{1}{2d}}{1 - \frac{1}{d}}, \tag{11}$$

which, in the mean-field limit, $d \to \infty$, coincide with y and c, Eq. (9).

(iv) Finally, the relaxation time is found to diverge at the threshold, $\tau_\epsilon \sim |\epsilon|^{-\zeta}$, with an exponent given by

$$\zeta = \frac{\beta x}{\tau - 2}\cdot \tag{12}$$

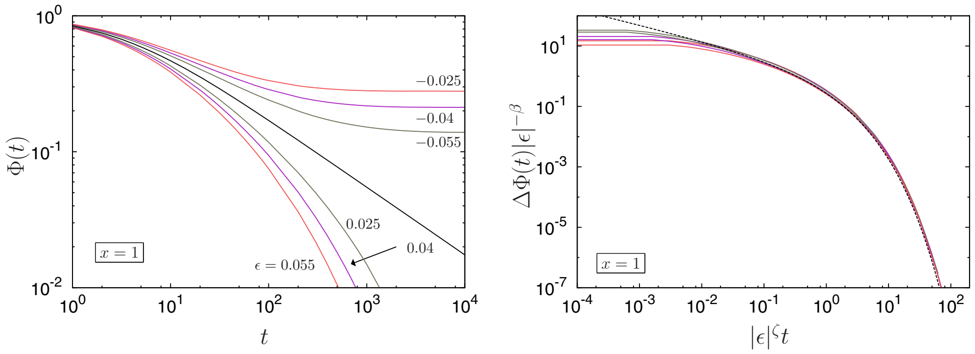

Fig. 1. Left: the correlator, $\Phi(t)$, with $x = 1$, evaluated from Eq. (5), for the bond percolation on a Bethe lattice of coordination number 4 (for which the percolation threshold is $p_c = 1/3$), at $p = 0.315$, 0.32, 0.325, $1/3$, 0.3417, 0.3467, 0.3517 (corresponding to $\epsilon = -0.055$, -0.04, -0.025, 0, 0.025, 0.04, 0.055). Right: rescaled non-arrested part of correlator vs. rescaled time, $|\epsilon|^2 t$, at $\epsilon = \pm 0.055$, ± 0.04, ± 0.025. Dashed line is given by Eq. (8), with $c = y = 1/(x+1) = 1/2$.

Such calculations are in agreement with the theoretical predictions obtained in Ref. [27–29] in the Rouse and Zimm models for randomly cross-linked monomers, where $x = 1$ and $x = 1/2$, respectively, and were confirmed in Ref. [19] by measuring the self-intermediate scattering function in molecular dynamics simulations of a model for permanent gels, where bonds between monomers are described by a FENE potential [30–36].

In mean-field, the critical exponents are $\beta = 1$ and $\tau = 5/2$. Moreover, using the exact results on the cluster size distribution of Ref. [37], the expression Eq. (5) can be exactly evaluated for any value of the bond occupation probability, p. In Fig. 1(left), we show the numerically computed $\Phi(t)$ for $x = 1$ and different values of p.

In Fig. 1(right), the rescaled correlator, $\Delta\Phi(t)/|\epsilon|$ is plotted versus the rescaled time, $t\,|\epsilon|^\zeta$ (with $\zeta = 2x = 2$, and $a = 1/2x = 1/2$), for different values of the bond occupation probability. Notice that $\Delta\Phi(t)$ is the non-arrested part of the correlator, which coincides with $\Phi(t)$ in the fluid phase, and with $\Phi(t) - P_\infty$ in the frozen phase, where P_∞ goes to zero linearly at the threshold, $P_\infty \sim |\epsilon|$, with $\epsilon = (p - p_c)/p_c$. As expected, after an initial transient, the curves collapse on a unique curve, which is well fitted by the theoretical expression, Eq. (8), with exponents $c = y = 1/(x+1) = 1/2$.

4 Mode-coupling theory for the continuous glass transition

The mode-coupling theory (MCT) (for a review, see [38]) is considered one of the most comprehensive first-principles approaches to the relaxation dynamics of supercooled liquids. Since its first appearance, however, the nature of the singularity predicted by MCT has been much debated because it appears as an artifact of uncontrolled approximations (and therefore it should actually represent a dynamic crossover). In spite of this and other limitations, several predictions of MCT have been substantially confirmed in real systems at qualitative and sometimes quantitative level (e.g. for short-range attractive colloids). MCT generally predicts that the glass transition is unrelated to any thermodynamic singularity and that the nature of this dynamic glass transition can be either continuous (type A) or discontinuous (type B).

Since the gel state is structurally disordered and gelation is a continuous transition one would reasonably expect that the percolation predictions outlined in the previous section be consistent with the MCT of type A glass transition. This is not obvious a priori since no reference to clusters is made in MCT. In order to address this issue we now briefly review the MCT framework and then compare with the percolation approach in the next section.

In MCT the time evolution of the correlator of density fluctuations, $\Phi(t)$, obeys the integro-differential equation:

$$\Phi(t) + t_0\,\dot{\Phi}(t) + \int_0^t \mathsf{M}[\Phi(t-s)]\;\dot{\Phi}(s)\,\mathrm{d}s = 0. \tag{13}$$

This equation is obtained by using the Zwanzig–Mori projection formalism applied to Langevin equation of motion. An additional inertial term would appear if we were using Newton equation of motion as a starting point. We denote with t_0 the characteristic timescale of the microscopic motion and, for simplicity, we neglect the wave-vector dependence of $\Phi(t)$. The memory kernel functional $\mathsf{M}[\Phi(t-s)]$ accounts for the caging of a particle by its neighbors. It depends smoothly on the static structure factor and does not involve any thermodynamic singularity. In the high temperature or low-density limit, the memory kernel is substantially negligible and therefore relaxation is exponential. At sufficiently high-density or low-temperature, instead, the nonzero value of the memory kernel causes a viscosity increase that through a feedback mechanism eventually leads to the structural arrest of dynamics. This means that the long-time limit of $\Phi(t)$ remains finite as the system keeps some memory of its initial state, i.e., it is a glass.

To obtain quantitative predictions about the general features of relaxation dynamics and the shape of the phase diagram, one can study schematic models in which the memory functional is represented by a low-order polynomial of correlators, with coupling constants that depend solely on the static structure factor. The two most studied cases are the F_{12} and F_{13} schematic models. In the first model, the memory kernel is represented as the superposition of a linear term and a quadratic term: $\mathsf{M}_{12}[\Phi(t)] = v_1\Phi(t) + v_2\Phi^2(t)$, while in the second model the quadratic term is replaced by a cubic one, $\mathsf{M}_{13}[\Phi(t)] = v_1\Phi(t) + v_3\Phi^3(t)$. The coupling parameters v_1, v_2 and v_3 control the system state and by changing their value a glass transition can be obtained. The key quantity to locate this transition is the non-ergodicity parameter, that is the long-time limit of the correlator, $q = \lim_{t\to\infty}\Phi(t)$, also known as the Edwards–Anderson parameter in the spin-glass literature. In the fluid state, when the system is ergodic, $\Phi(t)$ decays to zero and $q = 0$. When q is finite, the system is unable to fully relax, its dynamics is arrested and the liquid becomes a glass. For schematic models, one can easily derive the liquid-glass phase diagram. Taking the long-time limit of Eq. (13), one obtains the bifurcation equation:

$$\frac{q}{1-q} = \mathsf{M}[q] \tag{14}$$

whose solutions give different kinds of ergodic-nonergodic transitions, continuous and discontinuous. In connection with the sol-gel transition, we are only interested in the continuous transition. Therefore, we restrict here our attention to this case. The phase diagrams of the schematic models introduced above are shown in the Fig. 2. The continuous transition line is, for both schematic models, represented by the segment across which q smoothly departs linearly from zero, $q \sim \epsilon$ (red full lines in figures).

Near the continuous transition line, the MCT makes several specific predictions. At the threshold, the correlator decays as a power law, $\Phi(t) \sim t^{-a}$, and the structural

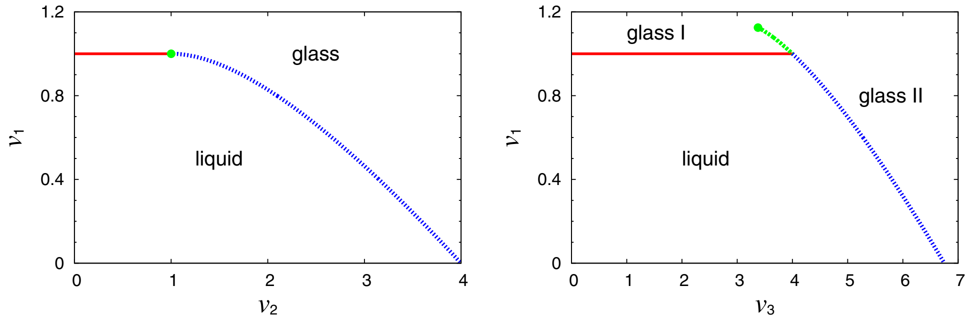

Fig. 2. Phase diagrams of schematic mode-coupling theory for the F_{12} (left) and F_{13} (right) models. Red full lines correspond to the continuous transitions.

relaxation time, τ_ϵ, at distance ϵ from the critical line, behaves as $\tau_\epsilon \sim |\epsilon|^{-\zeta}$ with an exponent ζ which is generally related to a by

$$\zeta = \frac{1}{a}\cdot \tag{15}$$

Furthermore, the exponent a can be related to the coupling parameters v_i.

In the F_{12} schematic model, the continuous transition line corresponds to the segment $v_1 = 1$ and $v_2 \in [0,1]$ (red full line in Fig. 2, left). Near the continuous transition [38], one gets

$$\frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = v_2, \tag{16}$$

where Γ is the Euler's gamma function.

In the F_{13} schematic model the continuous transition line corresponds to the segment $v_1 = 1$ and $v_3 \in [0,4]$ (red full line in Fig. 2, right). Again near the continuous transition, one gets:

$$\frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = 0. \tag{17}$$

The case $v_2 = v_3 = 0$, the so called F_1 model, is especially interesting because the time evolution of correlation function can be exactly computed [38]:

$$\Delta\Phi(t) = \frac{|\epsilon|}{2}\left[\sqrt{\frac{\tau_\epsilon}{\pi t}}\exp\left(-\frac{t}{\tau_\epsilon}\right) - \operatorname{erfc}\left(\sqrt{\frac{t}{\tau_\epsilon}}\right)\right], \tag{18}$$

where $\Delta\Phi(t)$ is the non-arrested part of the correlator and $\tau_\epsilon \simeq \epsilon^{-2}$ near the transition (with $\epsilon = 1 - 1/v_1$). The MCT results for this special case will be compared with the predictions of the dynamic percolation approach.

5 Comparison between cluster approach and mode-coupling theory

We are now in the position to compare the MCT results with the predictions obtained with the dynamic percolation approach at the mean field level.

First of all, the non-ergodicity parameter, $q = \lim_{t\to\infty}\Phi(t)$, approaches zero as $q \sim \epsilon^\beta$ with $\beta = 1$, which coincides with the mean-field value of the order parameter exponent of random percolation. This is the first hint suggesting the relevance of percolation in this context. In fact, MCT was originally developed to deal with the localization-diffusion behavior of the Lorentz gas (and the related problem of the conductor–insulator transition of quantum fluids in a random potential), a context

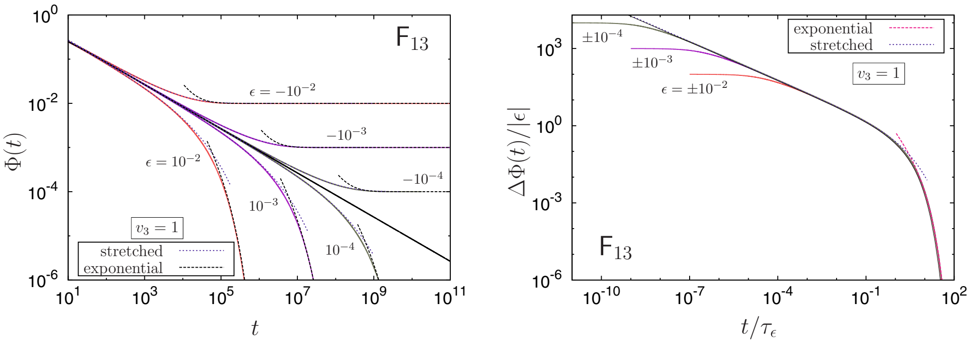

Fig. 3. Correlator (left) and its non-arrested part (right), $\Phi(t)$ and $\Delta\Phi(t)$, respectively, obtained numerically solving MCT Eq. (13), with memory kernel M_{13} and $v_3 = 1$. The dotted line is the stretched relaxation regime, Eq. (8), with exponents determined according to percolation predictions, Eqs. (7) and (9), $x = 1$, $c = y = a = 1/2$. The dashed line represents the late stage exponential decay.

in which percolation naturally appears. Secondly, from Eqs. (7) and (9), using the mean-field critical exponent, $\tau = 5/2$, mean-field universal relations can be derived:

$$\zeta\, a = 1, \qquad y = c = \frac{2a}{2a+1}, \tag{19}$$

where the first relation reproduces the second MCT relation, Eq. (15). Further, precise predictions can be obtained for the MCT solutions for the F_{12} model.

Near the continuous critical line, the correlator $\Phi(t)$ is expected to be characterized by an intermediate scaling regime given by Eq. (8), with exponents given by Eqs. (7) and (9) and x determined by

$$\frac{\Gamma^2(1-1/2x)}{\Gamma(1-1/x)} = v_2. \tag{20}$$

In particular this relation for $v_2 = 0$ gives $x = 1$ and consequently, from Eq. (19), $y = c = a = 1/2$ and $\zeta = 2$.

This prediction agrees with the exact solution, Eq. (18). Accordingly, at short times $t/\tau_\epsilon \ll 1$ relaxation is algebraic, $\Phi(t) \sim t^{-1/2}$, while at large times, $t/\tau_\epsilon \gg 1$, it is exponentially fast. Expanding Eq. (18), for small t/τ_ϵ, one finds:

$$\Delta\Phi(t) \simeq \frac{|\epsilon|}{2}\sqrt{\frac{\tau_\epsilon}{\pi t}}\left[1 - \sqrt{\frac{\pi t}{\tau_\epsilon}} + \frac{t}{\tau_\epsilon}\right], \tag{21}$$

that is, to the first leading order in $\sqrt{t/\tau_\epsilon}$, Eq. (8) with a normalized relaxation time $\tilde{\tau}_\epsilon = \pi\tau_\epsilon$. Thus the early and late stage relaxation behaviors are bridged by a scaling regime described by Eq. (8) with exponents exactly matched by the percolation predictions.

At intermediate times, data are well fitted by Eq. (8), with the exponents given above $x = 1$, $c = y = a = 1/2$. At long times, exponential decays are observed. Agreement is found also, by solving numerically the MCT equation for other values of v_2, for which the solution cannot be expressed in closed form [5], comparing with the cluster approach prediction with the corresponding values of x given by Eqs. (20).

Here, we have also found excellent agreement with the numerical MCT solutions for the F_{13} model along the continuous transition line for different values of v_3. Along this line the critical exponents do not change, and according to Eq. (17) they are all given by the same value $x = 1$ (see Fig. 3 for the particular case $v_3 = 1$). In Ref. [39], the possibility that the schematic MCT F_{13} model can describe mean field chemical gel is discussed in a model, where hard spheres are linked by permanent bonds with a given probability, p. To further analyze this connection, the above predictions can be easily checked along the percolation line.

6 Conclusions

After reviewing a cluster approach to the sol-gel transition, and the dynamical behavior of the continuous glass transition, as described by MCT, here we have presented some recent results, showing that MCT can be consistently interpreted as the infinite dimensional limit of the cluster percolation approach. This result has two interesting consequences. On the one hand, it shows that MCT is a suitable theory to describe the continuous transition to the arrested state occurring in gelation. On the other, this correspondence elucidates the geometrical character underlying MCT. This cluster approach thus provides new insight into the dynamical relaxation behavior and predicts a new intermediate stretched exponential regime in MCT with universal features.

A different behavior however is found in these two problems. The stretched exponential in the MCT extends only over an intermediate regime with a crossover to a simple exponential behavior in the long time regime, while in the cluster approach to chemical gelation the stretched exponential behavior extends forever. The reason for this latter behavior is related to the property of the bonds being permanent. The cluster approach introduced here thus applies to sol-gel transitions which are characterized by a free energy singularity, as in chemical gelation. If the bonds probability are instead characterized by a finite lifetime (but long compared to density relaxation), there is no singularity in the free energy, and the cluster approach would describe reversible gelation characterized by an intermediate stretched exponential followed by a simple exponential.

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