

## Glass-Glass Transition and New Dynamical Singularity Points in an Analytically Solvable $p$ -Spin Glasslike Model

Antonio Caiazzo, Antonio Coniglio, and Mario Nicodemi

Dipartimento di Scienze Fisiche, Università "Federico II," INFN-Coherentia and INFN Napoli, via Cintia, I-80126 Napoli, Italy

(Received 20 May 2004; published 15 November 2004)

We introduce and analytically study a generalized  $p$ -spin glasslike model that captures some of the main features of attractive glasses, recently found by mode coupling investigations, such as a glass-glass transition line and dynamical singularity points characterized by a logarithmic time dependence of the relaxation. The model also displays features not predicted by the mode coupling scenario that could further describe the attractive glasses behavior, such as aging effects with new dynamical singularity points ruled by logarithmic laws or the presence of a glass spinodal line.

DOI: 10.1103/PhysRevLett.93.215701

PACS numbers: 64.70.Pf, 05.50.+q, 64.60.Ht

Recent mode coupling theory (MCT) [1] investigations discovered [2] new kind of glasses, the so-called attractive glasses, characterized by the presence of a glass-glass transition line where higher order dynamical singularity points are located. As MCT calculations triggered intense experimental researches [3,4], their limit is that, by definition, they can correctly describe only the region outside the glass. In this Letter, we introduce a schematic  $p$ -spin glasslike model exhibiting a glass-glass transition which we can analytically investigated to establish the proper scenario of the glassy phase. This leads to new testable predictions on the aging dynamics in that region, where new types of singularities are found.

In MCT attractive glasses the potential between the particles presents attraction for some range besides the hard core repulsion [2]. Its volume fraction-temperature phase diagram shows two branches of the glass transition line, one due to the repulsive part of the potential, extending to high temperatures for volume fractions near the close packing value, and one related to the attraction, extending to low volume fractions up to meet the liquid-gas spinodal. For sufficiently narrow widths of the potential well one of the two branches interestingly enters in the glass region giving rise to a glass-glass transition line, ending in a higher order dynamical singularity point. This special point in the MCT framework is characterized by a logarithmic time dependence of the relaxation. The theory applies to attractive colloids; actually, some evidence of the MCT results has been found by recent experiments [3,4]. Nevertheless, for some aspects, the approach used in [2] turns out to be inadequate. It is known, in fact, that the MCT is valid only for equilibrium dynamics and cannot be trivially extended inside the glassy region, where the glass-glass line itself is located and aging phenomena are present. Another problem arises when the phase coexistence interferes with the glass transition line. In this case, the MCT does not allow a self-consistent description of the structural relaxation and the gas/liquid spinodal line is usually obtained *a priori*, not taking into account the presence of the

glassy phase. The purpose of the present work is to begin to cure these inconsistencies. Exploiting the strong analogies between glassy systems and the class of "discontinuous" spin glasses noticed in the last years [5], we introduce a schematic solvable model providing a coherent picture of the glass-glass line, its off-equilibrium dynamics and singularity points.

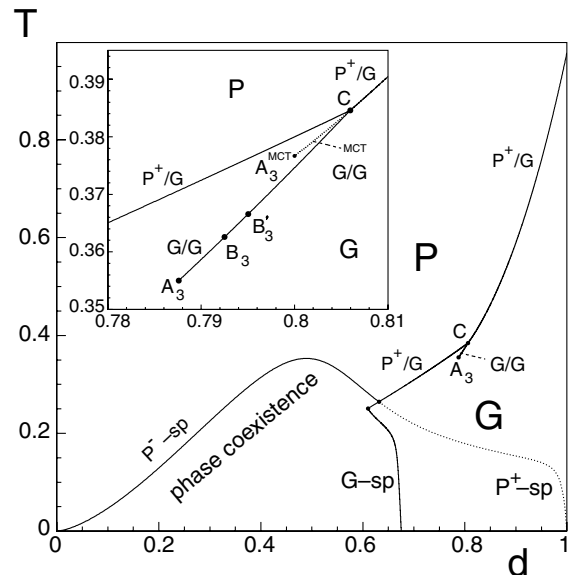


FIG. 1. The model dynamical phase diagram in the density-temperature plane (the parameters here are  $p_1 = 3$ ,  $p_2 = 11$ ,  $J_3^2 = 0.74$ ,  $J_{11}^2 = 4$ ,  $r = 12$ , and  $K_{12} = -12$ ). One can have a fluid ( $P$ ) phase consisting of gas ( $P^-$ ) and liquid ( $P^+$ ), or a glass ( $G$ ) phase. Continuous lines depict the liquid-glass ( $P^+/G$ ) and glass-glass ( $G/G$ ) transition lines, the spinodal of the fluid ( $P^-$ -sp and  $P^+$ -sp), and that of the glass ( $G$ -sp). The inset shows an enlargement of the region around the  $G/G$  transition line. The dotted line represents the incorrect  $G/G$  line predicted by MCT. On the  $G/G$  line (solid line from  $C$  to  $A_3$ ), along with its end point  $A_3$ , there are new dynamical singularity points,  $B_3$ ,  $B'_3$ , characterized by a logarithmic relaxation. Also the crossing point  $C$  between the two branches of the  $P^+/G$  transition line is shown.

The model consists of a combination of two (or more)  $p$ -spin models [6–8] diluted through density variables [9]. We analytically solve its Langevin dynamics and for comparison with the MCT inside the glassy region we also use the mode coupling approximation. We show that (i) the glass-glass transition line does not coincide with that predicted by the MCT but follows a different curve (Figs. 1 and 2). (ii) Along the glass-glass line (see Fig. 1) in the early regime the stationary autocorrelation function  $\Phi(t - t')$  exhibits, as in MCT, a power law relaxation, except at its end point  $A_3$  where it is logarithmic. (iii) In the long time regime, where the MCT predicts a plateau, we find an interesting aging dynamics. In particular, two more dynamical singularity points,  $B_3$  and  $B'_3$  (one for each kind of glass; see Fig. 1), characterize the relaxation in the aging regime. On one side of the glass-glass line from  $C$  to  $B_3$  (respectively  $B'_3$  on the other side; see inset of Fig. 1), the long times relaxation is a power law, except right at  $B_3$ , where it is logarithmic (analogously for  $B'_3$ ). From  $B_3$  (respectively  $B'_3$ ) to  $A_3$ , the aging behavior is spin glasslike [5]. (iv) Finally, at the  $A_4$  singularity (i.e., in the case where  $A_3$  coincides with point  $C$  in Fig. 1) we show that the logarithmic decay

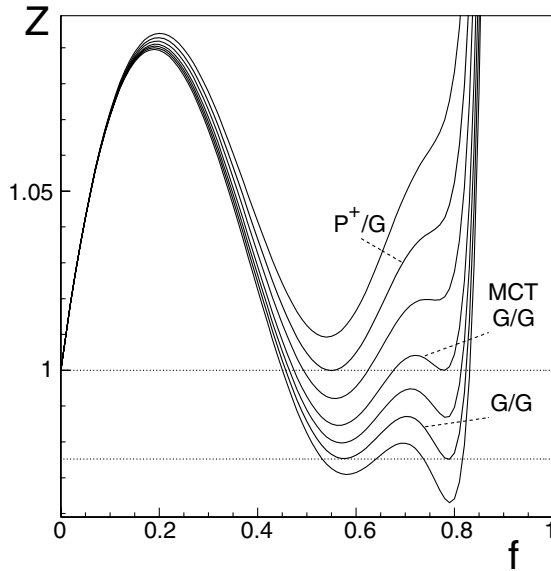


FIG. 2. The function  $Z(f)$  defined in Eq. (6) is plotted for several decreasing temperatures  $T$  (from top to bottom) and fixed density. For high  $T$  the liquid solution ( $P^+$ ) is given by the value  $f = 0$  corresponding to the lowest value of  $Z$ , namely,  $Z = 1$ . By lowering  $T$  the glass transition  $T_c$  is reached when the minimum of  $Z(f)$  approaches the level  $Z = 1$  (bold line marked  $P^+/G$ ). For  $T \leq T_c$  the plateau  $f_c$  is given by the value of  $f$  where  $Z(f)$  has the minimum. For low enough  $T$ ,  $Z(f)$  develops a second minimum. The  $G/G$  transition is reached when the two minima have the same depth (bold line marked  $G/G$ ). Note that in MCT approximation this would be reached instead when the second minimum approaches the level  $Z = 1$  (line marked  $G/G^{\text{MCT}}$ ).

of the correlation function in the stationary regime  $\Phi(t - t')$  is followed by an aging regime ruled again by a logarithmic law. (v) We calculate in a consistent way the density-temperature phase diagram and the spinodal lines (see Fig. 1) and find they are influenced by the presence of the glassy phase.

*The model.*—We consider a lattice gas model, where particles ( $n_i = 0, 1$ ) interact in groups of  $p$  via their spins ( $s_i = \pm 1$ ) through quenched random couplings  $J_{i_1, \dots, i_p}$ , with zero mean and variance  $p!J_p^2/(2N^{p-1})$ , and also in groups of  $r$  through (nonrandom) coupling constants  $K_r$  (typically, below we take two or three values of  $p$  and one value of  $r$ ). The mean field Hamiltonian is given by

$$H = -\sum_p \sum_{i_1 < \dots < i_p} J_{i_1, \dots, i_p} s_{i_1} n_{i_1} \dots s_{i_p} n_{i_p} - \sum_r \frac{r!K_r}{2N^{r-1}} \sum_{i_1 < \dots < i_r} n_{i_1} \dots n_{i_r} - \mu \sum_i n_i, \quad (1)$$

where  $\mu$  is the chemical potential. The spherical version of the model (1) is considered here: we introduce two new spin variables  $s_{ai}$  ( $a = 1, 2$ ), defined by  $s_i = s_{1i}$  and  $n_i = (s_{1i}s_{2i} + 1)/2$ , and enforce for these ones spherical constraints ( $\sum_i s_{ai}^2 = N$ ) [10]. To exclude the possibility of continuous transitions, not related to a glass transition, the restriction  $p > 2$  is taken [6]. The two spin fields  $s_{ai}$  ( $a = 1, 2$ ) evolve via usual Langevin equations with thermal noises  $\xi_{ai}(t)$ , having zero mean and variance  $\langle \xi_{ai}(t)\xi_{bj}(t') \rangle = 2T\delta_{ab}\delta_{ij}\delta(t - t')$ . Because of its quadratic nature, the model is exactly solvable. It has gas, liquid, and glassy phases called  $P^-$ ,  $P^+$  and  $G$ , respectively (see Fig. 1). We focus here on the dynamics, and, in particular, on the correlation function  $C(t, t') = \sum_{ia} \langle s_{1i}(t)s_{ai}(t') \rangle / (2N)$ , the related response function  $G(t, t')$ , and the density  $d(t) = C(t, t)$ . Standard functional techniques [7,11] allow one to derive the following dynamical equations for these quantities after a rapid quench at  $t = 0$  from high temperature ( $t \geq t'$ ):

$$\begin{aligned} \frac{\partial C(t, t')}{\partial t} &= -\frac{z(t)}{2} C(t, t') + 2TG(t', t) + \frac{1}{2} \\ &\times \int_0^{t'} du \varphi'[C(t, u)]G(t', u) + \frac{1}{2} \\ &\times \int_0^t du \varphi''[C(t, u)]G(t, u)C(u, t'), \quad (2) \end{aligned}$$

$$\begin{aligned} \frac{\partial G(t, t')}{\partial t} &= -\frac{z(t)}{2} G(t, t') + \frac{\delta(t - t')}{2} + \frac{1}{2} \\ &\times \int_{t'}^t du \varphi''[C(t, u)]G(t, u)G(u, t'), \quad (3) \end{aligned}$$

$$d'(t) = \{z(t) + 2\mu + 2\chi'[d(t)]\}[1 - d(t)] - T. \quad (4)$$

Here we define  $\varphi(x) = (1/2)\sum_p J_p^2 x^p$ ,  $\chi(x) = (1/2)\sum_r K_r x^r$ , and  $z(t) = z_1(t) - \mu - \chi'[d(t)]$ , with  $z_1(t) = z_2(t)$  the two time-dependent Lagrange multi-

pliers related to the spherical constraints (the prime stands for the first derivative). The above equations completely define the dynamical model, given the initial density  $d(0)$ . In the following we consider the large times limit, where one-time quantities reach stationary values:  $d = d(t \rightarrow \infty)$  and  $z = z(t \rightarrow \infty)$ .

*MCT calculations.*—Assuming equilibrium dynamics, we have that  $C = C(t - t')$  and  $G = G(t - t') \forall t, t'$  and the fluctuation-dissipation theorem (FDT) holds:  $TG(\tau) = -C'(\tau)$  (with  $\tau = t - t'$ ). Under these hypotheses, Eqs. (2) and (3) yield the long time schematic MCT equation [12] for the correlator  $\Phi(\tau) = C(\tau)/d$ ,

$$\tau_0 \frac{d\Phi(\tau)}{d\tau} + \Phi(\tau) + \int_0^\tau d\tau' m(\tau - \tau') \frac{d\Phi(\tau')}{d\tau'} = 0, \quad (5)$$

where  $m(\tau) = \varphi'[C(\tau)]d/T^2$ . In the standard MCT notation [1] the kernel  $m(\tau)$  is usually written as  $m(\tau) = F(\Phi(\tau), v)$ , with  $F(f, v) = \sum_n v_n f^n$ ; this allows one to establish a mapping relating  $T, d, J_p$  and the usual MCT control parameters  $v_n$ , given by  $v_n = pJ_p^2 d^p / (2T^2)$ , where  $n = p - 1$ . If  $p_1, p_2, \dots$ , denote the values assumed by  $p$ , we deal with the so-called  $F_{p_1-1, p_2-1, \dots}$  MCT model. The nonergodicity parameter  $f = \Phi(\tau \rightarrow \infty)$  is obtained by solving the bifurcation equation  $Z(f) = 1$  [i.e., the  $\tau \rightarrow \infty$  limit of Eq. (5)], where

$$Z(f) = \frac{1}{1-f} - F(f, v) = \frac{1}{1-f} - \sum_p \frac{pJ_p^2 d^p}{2T^2} f^{p-1}. \quad (6)$$

The inequality  $1 \leq Z[\Phi(\tau)]$ , deriving from the decreasing character of  $\Phi(\tau)$ , implies that  $f$  is the largest solution of the bifurcation equation [1]. The conditions  $Z(f_c) = 1$  and  $Z'(f_c) = 0$  determine the transition line in the plane  $d - T$  (see Fig. 1). The  $P^+/G$  transition, where  $f$  jumps from a zero to a nonzero value,  $f_c$ , corresponds to singularity points of type  $A_2$  [1]. MCT Eq. (5) describes the relaxation when this critical line is approached from the  $P^+$  phase:  $\Phi(\tau)$  decays in two steps characterized by power laws with critical exponents determined by the parameter  $\lambda = 1 - (1 - f_c)^3 Z''(f_c)/2 < 1$  [1]. Inside the glassy region, for a set of values of the parameters  $v_n$ , another line of  $A_2$  singularities appear (dotted line in the inset of Fig. 1) where two nonzero solutions for the dynamical order parameter,  $f$ , are allowed. This line defines the glass-glass ( $G/G$ ) transition, where a first glass,  $f_{c1}$ , transforms discontinuously into a second one,  $f_{c2}$  [1,2,13]. Its end point, where  $\lambda = 1$ , i.e.,  $Z''(f_c) = 0$ , results to be a higher order singularity  $A_3$  (with  $f_{c1} = f_{c2}$ ). To have a  $G/G$  line in our model, at least two values of  $p$  are needed [14]: as an example, for  $p_1 = 3$  the lowest other possible value is  $p_2 = 11$  (the case of Figs. 1 and 2).

*The glassy region and the new  $G/G$  line.*—Equation (5), i.e., MCT, is correct only out of the glassy phase (for  $f = 0$ ), where the equilibrium dynamics assumption holds. Thus, the above results on the  $G/G$  line are not correctly described by this theory. Within our model, we discuss

now the more complex nonequilibrium equations governing the glassy phase, the correct position of the  $G/G$  transition and the new aging behavior along the  $G/G$  line. In the glassy phase, as in the usual  $p$ -spin glass model, the relaxation of  $\Phi(t, t')$  can be split into two parts [5,8,11]: in the first part, describing the so-called FDT regime ( $t \approx t'$ ),  $\Phi(t, t')$  is a function,  $\Phi_{\text{FDT}}(\tau)$ , of the times difference  $\tau = t - t'$ ; the second part for  $t \gg t'$  corresponds to an aging regime described by a function  $\Phi_{\text{AG}}(t, t')$ . In the FDT regime, i.e., the approach of the correlator to the plateau  $f_c$ ,  $\Phi_{\text{FDT}}(\tau)$  satisfies the following equation:

$$\tau_0 \frac{d\Phi(\tau)}{d\tau} + Z\Phi(\tau) + (1 - Z) + \int_0^\tau d\tau' m(\tau - \tau') \frac{d\Phi(\tau')}{d\tau'} = 0, \quad (7)$$

where the existence of a well-defined aging solution fixes  $Z$  to the minimum value (not necessarily equal to 1) satisfying the stability requirement  $Z(f) \leq Z[\Phi_{\text{FDT}}(\tau)]$ , i.e., the one corresponding to the marginal stability condition  $Z'(f) = 0$  [8,11,15] (see Fig. 2). Note that Eq. (7) coincides with (5) only for  $Z = 1$ . The  $G/G$  transition line results is thus to be modified with respect to MCT and located by the conditions  $Z(f_{c1}) = Z(f_{c2})$  and  $Z'(f_{c1}) = Z'(f_{c2}) = 0$  (see Figs. 1 and 2). Its end point  $A_3$  (see Fig. 1) is characterized, as in MCT, by one more condition:  $f_{c1} = f_{c2} = f_c$  with  $Z''(f_c) = 0$ , corresponding to  $\lambda = 1$ .

In the aging region, the correlator  $C_{\text{AG}}(t, t') = \Phi_{\text{AG}}(t, t')d$  and the response function  $G_{\text{AG}}(t, t')$  obey a generalized FDT relation,  $TG_{\text{AG}}(t, t') = x \partial C_{\text{AG}}(t, t') / \partial t'$ , where  $x \leq 1$  is a constant with the physical meaning of the ratio between the bath temperature and an effective temperature  $T_{\text{eff}}$ , describing the out of equilibrium configurations  $x = T/T_{\text{eff}}$  [5].

*The dynamics along the  $G/G$  line.*—On the  $G/G$  line two glasses coexist corresponding to two different values of the plateau,  $f$ , and thus two different values of  $x = x(f)$  and  $\lambda = \lambda(f)$  (with  $0 \leq x \leq 1$  and  $0 \leq \lambda \leq 1$ ), except at the end point  $A_3$  where the glasses coincide. As shown below, along the line the value of  $\lambda$  determines the properties of the dynamics in the FDT regime, namely, the approach to the plateau, while the ratio  $\lambda/x$  determines the aging regime, i.e., the departure from the plateau. Four different behaviors are found along the  $G/G$  line (see Fig. 1): the case  $\lambda/x < 1$ , corresponding to the points from  $C$  to  $B_3$  (respectively  $B'_3$  on the other side of the line; see below); the new dynamical singularity points  $B_3$  and  $B'_3$  where  $\lambda/x = 1$ ; the case  $\lambda/x > 1$  extending from  $B_3$  (respectively  $B'_3$ ) to the end point  $A_3$ ; and the singular point  $A_3$  itself where  $\lambda/x > 1$ , but  $\lambda = 1$ .

More precisely, the approach to the plateau in the FDT regime, along the entire  $G/G$  line, is given by  $\Phi_{\text{FDT}}(\tau) - f_c \sim \tau^{-\beta}$ , where the exponent  $\beta$  is given by  $\Gamma^2(1 - \beta)/\Gamma(1 - 2\beta) = \lambda$  [5,8,11] ( $\Gamma$  is Euler gamma function).

At the end point  $A_3$  where  $\lambda = 1$  this is replaced by a logarithmic behavior given by  $\Phi_{\text{FDT}}(\tau) - f_c \sim 1/\ln^2\tau$  [1,2,13].

The departure from the plateau in the aging regime, along the  $G/G$  line from the crossing point  $C$  up to the two new points  $B_3$  and  $B'_3$ , one for each side of the line, is given by a power law:

$$\Phi_{\text{AG}}(t' + \tau, t') - f_c \sim -[\tau/\mathcal{T}(t')]^\alpha, \quad (8)$$

with  $\Gamma^2(1 + \alpha)/\Gamma(1 + 2\alpha) = \lambda/x$  [8]. Here the  $t'$  dependence is contained in  $\mathcal{T}(t') \sim t'$  [16].

At the two new dynamical singular points,  $B_3$  and  $B'_3$ , where  $\lambda/x = 1$ , this power law is replaced by a logarithmic behavior, one for each side of the  $G/G$  line. For instance, by approaching  $B_3$  from the right (the side where the plateau value  $f_c$  is higher) one has

$$\Phi_{\text{AG}}(t' + \tau, t') - f_c \sim 1/\ln^2[\tau/\mathcal{T}(t')]. \quad (9)$$

From the point  $B_3$  to the end point  $A_3$  (analogous to  $B'_3$  to  $A_3$  on the other side of the  $G/G$  line),  $\lambda/x > 1$ . This implies that the present one-step replica symmetry breaking solution should not hold [11] and, instead, a spin glasslike aging dynamics should be found in such a region [5].

Interestingly, the length of the  $G/G$  line can be varied and, in a version of the model with three  $p$  values [14], the  $A_3$  end point singularity can be made to coincide with the crossing point  $C$  (see Fig. 1). In this particular case, the  $A_3$  becomes an  $A_4$  singularity, as also found by MCT [2] (the simplest model with such a singularity is found to be  $p_1 = 3$ ,  $p_2 = 4$ , and  $p_3 = 11$  [14]). In this case, the FDT regime is logarithmic  $\Phi_{\text{FDT}}(\tau) - f_c \sim 1/\ln\tau$ , as in MCT [1,2,13], as well as the aging regime:

$$\Phi_{\text{AG}}(t' + \tau, t') - f_c \sim 1/\ln[\tau/\mathcal{T}(t')]. \quad (10)$$

*Spinodal lines.*—We show now that the glass transition curve  $P^+/G$  intersects the fluid spinodal line determining the existence of a glass spinodal line. The two spinodals are obtained by enforcing the vanishing local stability conditions in Eq. (4):

$$\beta^2 \varphi''(d) + 2\beta \chi''(d) - \frac{1}{(1-d)^2} - \frac{1}{d^2(1-f)^2} = 0. \quad (11)$$

The  $P^-/P^+$  spinodal corresponds to a solution,  $T(d)$ , with  $f = 0$ ; as for the  $G$ -spinodal solution, the value of  $f$  of the glassy phase is given by the marginal stability condition  $Z'(f) = 0$ . The two lines, completing the dynamical phase diagram, together with their range of validity are shown in Fig. 1.

In conclusion, the model we have introduced is a simple extension of  $p$ -spin glass models [6–8] for the glass transition. Our model exhibits a glass-glass transition line which can be analytically investigated. Actually, it

turns out to be different from the  $G/G$  line derived by equilibrium MCT and to be characterized by new dynamical singularity points and off-equilibrium properties. These results can help to shed light on the properties of attractive glasses, such as colloidal suspensions.

This work is supported by MIUR-PRIN 2002, FIRB 2002, CRdC-AMRA, INFM-PCI, and EU MRTN-CT-2003-504712.

- 
- [1] W. Götze, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North Holland, Amsterdam, 1991); W. Götze and M. Sperl, Phys. Rev. E **66**, 11405 (2002); J. Phys. Condens. Matter **15**, S869 (2003); M. Sperl, cond-mat/0310772.
  - [2] K. Dawson *et al.*, Phys. Rev. E **63**, 11401 (2001); E. Zaccarelli, G. Foffi, K. Dawson, F. Sciortino, and P. Tartaglia, Phys. Rev. E **63**, 31501 (2001).
  - [3] F. Mallamace *et al.*, Phys. Rev. Lett. **84**, 5431 (2000); W. R. Chen, S. H. Chen, and F. Mallamace, Science **300**, 619 (2003).
  - [4] T. Eckert and E. Bartsch, Phys. Rev. Lett. **89**, 125701 (2002); K. N. Pham *et al.*, Science **296**, 104 (2002); W. C. K. Poon, K. N. Pham, S. U. Egelhaaf, and P. N. Pusey, J. Phys. Condens. Matter **16**, S269 (2003).
  - [5] J. P. Bouchaud, L. F. Cugliandolo, J. Kurchan, and M. Mezard, in *Spin Glasses and Random Fields*, edited by A. P. Young (World Scientific, Singapore, 1997).
  - [6] Th. M. Nieuwenhuizen, Phys. Rev. Lett. **74**, 4289 (1995); S. Ciuchi and A. Crisanti, Europhys. Lett. **49**, 754 (2000).
  - [7] H. Sompolinsky and A. Zippelius, Phys. Rev. B **25**, 6860 (1982); T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. B **36**, 5388 (1987).
  - [8] L. F. Cugliandolo and J. Kurchan, Phys. Rev. Lett. **71**, 173 (1993).
  - [9] J. Aizenberg, M. Nicodemi, and M. Sellitto, J. Phys. I (France) **6**, 1143 (1996); **7**, 945 (1997).
  - [10] A. Caiazzo, A. Coniglio, and M. Nicodemi, Phys. Rev. E **66**, 46101 (2002); Europhys. Lett. **65**, 256 (2004).
  - [11] L. F. Cugliandolo and P. Le Doussal, Phys. Rev. E **53**, 1525 (1996).
  - [12] The full MCT equation also contains a second-order time derivative term [1]. Since it becomes negligible at large times, it is often ignored in literature, as explained in [5].
  - [13] W. Götze and M. Sperl, Phys. Rev. E **66**, 11405 (2002); M. Sperl, J. Phys. Condens. Matter **16**, S4807 (2004).
  - [14] Detailed calculations will be reported in a longer paper by A. Caiazzo, A. Coniglio, and M. Nicodemi (to be published).
  - [15] H. Kinzelbach and H. Horner, J. Phys. I (France) **3**, 1329 (1993); **3**, 1901 (1993); S. Franz and M. Mezard, Physica (Amsterdam) **209A**, 1 (1994); A. Crisanti, H. Horner, and H. J. Sommers, Z. Phys. B **92**, 257 (1993).
  - [16] More precisely,  $\mathcal{T}(t') = h(t')/h'(t')$ , where  $h(t)$  is a time reparametrization increasing function (for the  $p$ -spin glass model one can assume  $h(t) \sim t$ ; see [8]).