Critical dynamical heterogeneities close to continuous second-order glass transitions

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We analyse, using Inhomogenous Mode-Coupling Theory, the critical scaling behaviour of the dynamical susceptibility at a distance \( \epsilon \) from continuous second-order glass transitions. We find that the dynamical correlation length \( \xi \) behaves generically as \( \epsilon^{-1/3} \) and that the upper critical dimension is equal to six. More surprisingly, we find activated dynamic scaling, where \( \xi \) grows with time as \( \ln^2 t \) exactly at criticality. All these results suggest a deep analogy between the glassy behaviour of attractive colloids or randomly pinned supercooled liquids and that of the Random Field Ising Model.

Several recent studies have revealed that the properties of the glass transition can be drastically modified by suitably tuning some control parameters. In the case of the colloidal glass transition, an attractive interaction on top of the hard-sphere repulsion can change the dynamical behaviour and lead to glass-glass transitions and logarithmic relaxation \([1]\). This behaviour is also expected for glassy liquids in porous media \([2]\). For generic glass-forming liquids, it was recently predicted \([3, 4]\) that randomly pinning a fraction of particles would transmute the glass transition in a continuous second-order phase transition akin to that of the Random Field Ising model (RFIM) \([3, 5]\). There are strong theoretical indications that these phenomena are in fact all related to the existence of a new kind of glassy critical point, first found within Mode-Coupling Theory (MCT) as a higher-order singularity \([6]\). The physical contexts in which it appears are quite different: for attractive colloids it is a terminal point of a glass-glass transition line, for glass-forming liquids either pinned or trapped in porous media it corresponds to the locus where the Mode-Coupling transition and the Ideal Glass transition lines merge. In the former case the glass transition line stops at this new critical point \([5]\), whereas in the latter it carries on and becomes continuous \([2]\). Remarkably, in all these physical situations, activated processes not described by MCT are either suppressed, since the region where they appear shrinks to zero for glass-forming liquids, or not relevant since the system is in the glass phase for attractive colloids. Hence, MCT might become quantitatively accurate in these situations. The dynamical behaviour of the two-point functions at this new glassy critical point, that we will call A3 using Götze’s terminology, was predicted by MCT computations \([6]\) and confirmed later both numerically and experimentally in colloids \([1]\). The static properties of the fluctuations of the overlap field between two equilibrium configurations were recently investigated in \([3, 4]\) and, using simulations, in \([7]\). A complete theory of dynamical correlations is however still lacking. The aim of this paper is to develop such a theory by extending the “Inhomogeneous” MCT (IMCT) formalism, which was developed by some of us \([8]\) to describe dynamical heterogeneities at the usual MCT transition. We shall obtain the mean-field values of the critical exponents, the upper critical dimension and derive the critical behavior, which turns out to be very different from the usual one. We find in particular activated dynamic scaling, which strongly bolsters the relationship with the RFIM \([3, 5]\).

In order to grasp the main properties of the A3 critical point, it is useful to focus on the mean-field Landau-like potential \( V(f; \epsilon) \), called the Franz-Parisi (FP) potential in the present context \([3]\). The arguments \( \epsilon \) and \( f \) are, respectively, the vector of all control parameters that can be tuned (e.g. the temperature and the fraction of pinned particles) and the glassy (non-ergodic) order parameter, which measures how far the dynamics can displace the system away from its initial configuration. For usual glass transitions, the FP potential has a unique minimum \( f_0 = 0 \) at high temperatures; it corresponds to a complete loss of memory of the initial condition as normal in a liquid. A secondary minimum appears for \( f = f^* > 0 \) below a certain transition temperature \( T_c \), see Fig. 1. An important achievement of the last decades was to establish that \( T_c \) actually coincides with the MCT transition, where locally stable, long-lived amorphous structures, corresponding to the secondary minimum of \( V(f; \epsilon) \), appear. Roughly speaking, the connection between the FP potential and MCT may be expressed as \( V'(f; \epsilon) = \overline{F}_0 - F_q[f] \), where \( F_q[f] \) is the memory function of the MCT equations (The full-fledged MCT calculation deals with wave-vector dependent order parameters \( f_q \), we will return to this below) \([10]\). An A3 critical point corresponds to the merging of the minima \( f_0 \) and \( f^* \) \([11, 12]\). It is of co-dimension 2, much as the liquid-gas critical point, i.e. one needs to tune at least two control parameters to reach it, as found for systems with quenched pinning sites (see inset of Fig. 1) and for hard sphere systems, where one tunes the short-range attractive interactions and the density.

Technically, the existence of an underlying thermody-
The two special directions mentioned in the text are shown.

Namical formulation has been extremely useful to understand that the MCT transition is necessarily accompanied by the divergence of a length scale, which governs the spatial extent over which dynamical fluctuations are correlated, a feature that was hard to anticipate within the original framework of Götze et al. This diverging length scale is in fact a direct consequence of the vanishing of the curvature $V''(f; \varepsilon)$ of the FP potential at $T_c$ (see Fig. 1) \cite{13, 15}. The IMCT formalism allowed us to make a series of precise predictions about the space-time scaling of dynamical heterogeneities in supercooled liquids close to $T_c$ \cite{8}. One finds in particular that the dynamical correlation length diverges as $|T - T_c|^{-1/4}$ as the critical point is approached. Although the IMCT predictions are only expected to be correct far enough from $T_c$ below 8 dimensions, many general predictions appear to be confirmed, sometimes quantitatively, by large scale computer simulations, see \cite{16} and refs therein. These developments, and others, strongly support a quantitative theory of supercooled liquids built using the mean-field scenario as a starting point, much as Curie-Weiss theory provides a foundation for the modern theory of critical phenomena \cite{17, 18}.

In the following we first explain our results in an informal and simple way based on the behaviour of the FP potential; we then sketch the complete IMCT derivation. We will denote as $V^{(n)}$ the $n$-th derivative of $V(f; \varepsilon)$ with respect to $f$ ($V'' = V^{(1)}$, etc.), and $\nabla_\varepsilon V$ the gradient of $V$ with respect to the parameters. The expansion of $V'(f; \varepsilon)$ around the transition point $f = f_c$, $\varepsilon = 0$ reads, with $\delta f = f - f_c$: \[ V'(f; \varepsilon) \approx V_c^{(2)} \delta f + \frac{1}{2} V_c^{(3)} \delta f^2 + \frac{1}{3} V_c^{(4)} \delta f^3 + \nabla_\varepsilon V_c' \cdot \varepsilon + \nabla_\varepsilon V_c^{(2)} \cdot \varepsilon \delta f + \ldots, \]

where we have used that by definition, at the transition, \[ V'(f_c; 0) = 0. \] The standard MCT transition (the A2 critical point) occurs when the secondary minimum of $V(f)$ just appears, implying $V_c^{(2)} = 0$ (see Fig. 1). The next order singularity (A3) occurs when $V_c^{(3)}$ concomitantly vanishes as well (see Fig. 1). Looking for the new location $f^*$ of the minimum away from the transition, one finds, to leading order in $\varepsilon = |\varepsilon|$: $f^* - f_c \approx \sqrt{\varepsilon}$, as is familiar for the A2 case and $f^* - f_c \approx \sqrt{\varepsilon}$ in the generic A3 case. There is however a subtlety here: since the A3 point requires at least two parameters to be varied simultaneously, one needs to include the case where the chosen trajectory in parameter space is precisely perpendicular to $\nabla_\varepsilon V_c'$, in which case one finds again the weaker singularity $f^* - f_c \sim \sqrt{\varepsilon}$, where $\varepsilon_{\perp}$ is the distance to the critical point along that special direction. The motivation for the notation $\varepsilon_{\perp}$ stems from the liquid-glass phase diagram, sketched in the inset of Fig. 1 in the case of random pinning glass transitions \cite{8}. In general A3 is the terminal point of the line of A2 critical points. The special direction found above is the one tangent to the A2 line. In consequence, we also introduce the notation $\varepsilon_{\perp}$ for the magnitude of the component of $\varepsilon$ perpendicular to the A2 line (i.e. parallel to $\nabla_\varepsilon V_c'$).

The main idea of IMCT \cite{8} is to perturb the system with a small spatially periodic external potential $\propto \cos(\varphi_0 \cdot \vec{x})$, whose spatial profile varies over the length-scale $1/\varphi_0$. The characteristic value of $\varphi_0$ at which the external perturbation starts to act differently from a uniform, $\varphi_0 = 0$, perturbation allows one to obtain the correlation length of dynamical heterogeneities as $\xi = 1/\varphi_0$. Since all the physics of the slowing down is governed by the vanishing of the curvature of the FP potential, the crucial point is to work out how the periodic perturbation (of zero mean) changes this curvature. Because the system is rotationally invariant, it is reasonable to assume that the extra contribution to the curvature is $\sim \varphi_0^2$. Therefore, one has: \[ V''(f^*; \varepsilon) \approx V_c^{(3)}(f^* - f_c) + \frac{1}{2} V_c^{(4)}(f^* - f_c)^2 + \nabla_\varepsilon V_c^{(2)} \cdot \varepsilon + \Gamma \varphi_0^2. \]

Close to an A2 critical point, $V_c^{(3)} \neq 0$ and $f^* - f_c \sim \sqrt{\varepsilon}$, which shows that the characteristic value of $\varphi_0$ beyond which the relaxation time substantially changes is $\sim \varepsilon^{1/4}$, leading to $\xi \sim \varepsilon^{-1/4}$, in agreement with the result of \cite{8}. Upon approaching an A3 critical point, $V_c^{(3)} = 0$, leading to $\xi \sim \varepsilon_{\perp}^{-1/3}$ in the generic case, and to $\xi \sim \varepsilon_{\perp}^{-1/2}$ in the special case where $\varepsilon_{\perp} = 0$. These results are fully confirmed, and made more precise, by the IMCT analysis that we now briefly present.

The IMCT formalism starts from an exact equation for the inhomogeneous dynamic structure factor $F(q_1, q_2, t) = \langle \rho_{q_1}(t) \rho_{-q_2}(0) \rangle$ in the presence of an inhomogeneous external field $u(q_0)$:

\[
\frac{\partial F(q_1, q_2, t)}{\partial t} + \Omega_q F(q_1, q_2, t) + \sum_k \int_0^t M(q_1, k, t - t') \times \frac{\partial F(k, q_2, t')}{\partial q_1} \, dt' = T_u(q_1, q_2, t),
\]
where $\Omega_{q_1} \equiv q_1^2 k_B T / S_{q_1}$ is a frequency term, $M(q_1, k, t)$ is the memory kernel and $\tau_m(q_1, q_2, t)$ contains all the terms generated due to the external potential. The dynamical susceptibility is defined as $\chi_{q_0}(q_1, t) = \delta F(q_1, q_1 + q_0, t) / \delta u(q_0) |_{u \to 0}$. This object obeys a linear equation (that we do not write here, see [8]) obtained by taking the derivative of Eq. (1) with respect to $u(q_0)$. In the long-time limit, this linear equation reads:

$$\sum_k \left( \delta_{k, q} - C_{q, k}(q_0) \right) \chi_{q_0}(k, t \to \infty) = S(q, q_0),$$

where $S(q, q_0)$ is a non singular source term and $C_{q, k}(q_0)$ is a $q_0$ dependent matrix that can be fully computed in terms of the memory kernel of the external potential. In order to analyse Eq. (2) we recall (see [11]) that $C_{q, k}(0) = (1 - f_k)^2 \partial F_q \epsilon \langle \{ f_k \} \rangle / \partial f_k$. The properties of the operator $\delta_{k, q} - C_{q, k}(0)$, which is akin to $V'(f; \epsilon)$, are reported in [11]: at distance $\epsilon$ from the transition, one finds $f_k = f_k^\pm (1 - f_k^2)^2 g_k$, where $g_k \propto \sqrt{\epsilon} v_k^R$ and $v_k^R$ is the (right) zero mode of $\hat{A}$ evaluated at the transition point. This scaling holds when approaching the A3 critical point in any direction other than the one parallel to the line of usual A2 transitions that approach the A3 point. In this case one finds $g_k \propto \sqrt{\epsilon} v_k^R$. Away from criticality, the smallest eigenvalue of the matrix $\hat{A}$ is not exactly zero: the deviations are of order, respectively, $\epsilon^{2/3}$ and $\epsilon$ close to an A3 point, depending on the direction of approach to criticality. Coming back to our original problem, we remark that the eigenvalues of $C_{q, k}(q_0)$ can be computed using perturbation theory. Due to rotational invariance, one finds that all eigenvalues of $C_{q, k}(0)$ are shifted by an amount $\propto \epsilon^2_0$. The smallest eigenvalue of $\hat{A} - \hat{C}(q_0)$ is therefore equal to $\alpha / |\epsilon|^{2/3} + \Gamma^2_0$, where $\alpha$ and $\Gamma$ are numbers, and $\epsilon \neq 0$. The solution of Eq. (2) will be dominated by this very small eigenvalue, and thus reads:

$$\chi_{q_0}(k, t \to \infty) \approx \frac{\langle \psi^L | S \rangle \psi_k^R}{\alpha / |\epsilon|^{2/3} + \Gamma^2_0},$$

where $\psi^L, R$ are the left and right largest eigenvectors of $C_{q, k}$ at criticality. From this expression, one directly demonstrates the existence of a diverging susceptibility and a diverging length scale within MCT, which is intimately due to the vanishing of the curvature of the FP potential. Close to an A3 point, this length scale diverges as $|\epsilon|^{-1/3}$, as announced above. The time dependent analysis is more cumbersome and will be presented in detail elsewhere [22]. The final result is:

$$\chi_{q_0}(k, t) \sim \frac{V_{\parallel}(k) \xi^L_{\parallel} / \xi_{\perp}}{1 + \Gamma (q_0 / \xi_{\perp})^2} G_{\parallel} \left( \frac{t}{\sqrt{\xi_{\perp}} q_0 \xi_{\parallel}} \right), \quad \epsilon \neq 0,$$

$$\chi_{q_0}(k, t) \sim \frac{V_{\perp}(k) \xi^L_{\perp} / \epsilon}{1 + \Gamma (q_0 / \xi_{\perp})^2} G_{\perp} \left( \frac{t}{\sqrt{\xi_{\perp}} q_0 \xi_{\parallel}} \right), \quad \epsilon = 0,$$

where $V_{\parallel, \perp}(k)$ are certain functions, and $\xi_{\parallel} = |\epsilon|^{-1/3}$, $\xi_{\perp} = |\epsilon|^{-1/2}$, as indicated already by the simple arguments above.

The scaling functions $G_{\parallel, \perp}(u, v)$ are such that in the limit $\epsilon \to 0$ and $q_0 = 0$ (corresponding to a uniform perturbation), the dynamical susceptibility is well defined. This imposes $G_{\parallel, \perp}(u, v = 0) \sim u^4$, and therefore, at criticality, $\chi^0_{\parallel, \perp}(k, t) \sim t^4$, a result that can be obtained directly by taking the derivative of the scaling function of $F(k, t)$ close to an A3 critical point, see [11], and that is compatible with the simulation results of attractive colloids reported in [10]. Away from criticality, the $t^4$ behaviour only persists up to a time $\tau_\xi$ such that $\ln \tau_\xi \sim \sqrt{\epsilon_0}$ (or $\ln \tau_\xi \sim \sqrt{\xi_{\perp}}$ along the special line $\epsilon = 0$). Note that the exponential dependence of the relaxation time as a function of the distance from the critical point was already known from the critical behaviour of the dynamical structure factor, see [11].

Another interesting limit is when the system is critical $\epsilon_{\perp, \parallel} = 0$ and perturbed at a non-zero spatial frequency, $q_0 \neq 0$. In order to retain a non-trivial dynamics, one must now have $G_{\parallel, \perp}(u \to 0, v \to \infty) = g(u^2v)$, where $g(x)$ is a certain function behaving as $x^2$ for small $x$, and saturating to a constant for $x \to \infty$. This leads to: $\chi_{q_0}^c(k, t) = q_0^2 g(q_0 \ln^2 t)$, which shows that at criticality, the dynamical length grows without bound, as $\xi_{\parallel}(t) \sim t^{\beta}$. This should be compared with the corresponding result for the A2 point, where $\xi \sim t^{\beta/2}$, where $\beta$ is the MCT exponent for the $\beta$-regime. As the A3 point is approached, the value of $\alpha$ tends to zero and
the power law crosses over to a logarithmic behaviour. Note that there is no α-regime at the A3 point, contrarily to the usual phenomenology of the A2 transition. In the latter case, the $q_0$ dependence of $\chi_{q_0}$ for $q_0 \gg \xi^{-1}$ crosses over from $q_0^{-2}$ in the short time, β-regime, to $q_0^{-4}$ in the long time, α-regime. For the A3 transition, on the other hand, only the $q_0^{-2}$ behaviour survives. We have checked all these results numerically by solving exactly the dynamical equation obeyed by $\chi_{q_0}(t)$ in the so-called schematic limit where all k dependence is discarded. We have chosen the $F_{13}$ model for which the memory kernel is $F_2(f) = \epsilon_1 f + \epsilon_3 f^3$. The salient features of the above scaling predictions for $\chi_{q_0}(t)$ are confirmed in Fig. 2. From a purely phenomenological point of view, the most important points are: (1) the growth of $\chi_{q_0}$ is a logarithmic function of the relaxation time thus implying that dynamical heterogeneities increase much slower close to an A3 critical point than close to an A2 one; this might explain the numerical data of [21]; (2) the shape of $\chi_{q_0}$ is markedly different from the one found at an ordinary MCT transition. In particular, both the maximum and the long-time limit of $\chi_{q_0}$ diverge as the transition is approached, at variance with what happens close to an A2 point, where the long-time limit of $\chi_{q_0}$ remains bounded.

All the above results should be only be valid in high enough dimensions. In order to assess the effect of critical fluctuations on mean-field results one has to focus on the 4-point density correlations often called $G_4(r)$, which is related (in Fourier space) to the square of the dynamical susceptibility $\chi_{q_0}$ defined above (see [22] for a full justification of this relation). Since $\chi_{q_0}$ behaves as $q_0^{-2}$ at criticality, $G_4(r)$ is found to decay as $1/r^{d-4}$ up to distances of order $\xi$. This allows one to estimate the intensive fluctuations of the order parameter $f^*$ in a region of size $\xi^d$, which is found to be $\sqrt{2\beta f^2} \sim \xi^{-(d-\beta)/2} = \nu^{(4-d)/2}$, which must be compared to $f^* - f_c \sim \epsilon^\beta$. Since $\beta = \nu = 1/3$ for A3 transitions (or $\beta = \nu = 1/2$ along the special direction) we conclude that the upper critical dimension $d_\nu$ below which critical fluctuations change the nature of the transition is $d_\nu = 6$, instead of $d_\nu = 8$ as found for usual MCT transitions [22, 24]. Therefore, in physical dimensions $d = 3$, one expects that these critical fluctuations will considerably affect the above predictions, at least close enough to the critical point. The relative influence of these fluctuations, and the quantitative size of the Ginzburg region where critical fluctuations are strong, are expected to depend on the model. But one consequence of these fluctuations that is physically relevant is the violation of the Stokes-Einstein relation, relating the relaxation time of the system to the diffusion constant of probe particles. Simulations of thermal and athermal [22, 28] systems appear to conform to the prediction $d_\nu = 8$ for usual MCT transitions, yielding, for example, a Stokes-Einstein violation exponent that vanishes linearly as $8 - d = 20$. Our above analysis demonstrates that near an A3 singularity the upper critical dimension of fluctuations is shifted down to a value $d_\nu = 6$. This result is indeed qualitatively consistent with the fact that some aspects of dynamical heterogeneity (such as bimodality of particle displacement distributions) are suppressed as one tunes, via the introduction of short-ranged attractions, a supercooled hard-sphere suspension to a regime dominated by higher-order singularities [27]. More numerical work on this and other aspects of our theory would be welcome, using simulations of attractive hard-spheres in higher dimensions, along the lines of [28].

Finally, the alert reader will have recognized, both from the evolution of the FP potential shown in Fig. 1 and the value of the exponent $\beta = 1/3$ in generic directions and $\beta = 1/2$ in a special direction, that the A3 critical point is akin to an Ising transition, where $\epsilon_\parallel$ is a magnetic-field-like perturbation and $\epsilon_\perp$ is a temperature-like perturbation. The behaviour of the correlation function $G_4(r) \sim r^{4-d}$ and the corresponding value $d_\nu = 6$ points towards the universality class of the RFIM, in line with previous static treatments [3, 5]. Indeed, the A2 line is analogous to the spinodal line of the RFIM [24], which terminates at the A3 RFIM critical point. Remarkably, the logarithmic behaviour of the correlation function and of the dynamical correlation length that we found is usually a manifestation of activated events, which are indeed expected for the RFIM at criticality, but were thought to be impossible to grasp within an MCT formalism [19]. On the other hand, as mentioned above, cooperative activated processes not described by MCT are either suppressed or not relevant at an A3 critical point, thus opening the possibility that above $d > 6$ MCT indeed captures the correct behaviour. Curiously, however, the dynamical behaviour of the RFIM in high dimensions has not been worked out yet. Usual scaling arguments leading to $\log \tau \propto \xi^\theta$ (where $\theta$ is the stiffness exponent) are expected to break down above $d = d_{DR} \simeq 5.1$ [24]. Understanding what extent dynamic scaling holds above $d_{DR}$ and comparing the actual RFIM dynamical behaviour above six dimension to the prediction of MCT near an A3 point is certainly a topic worth a further studies.

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Note that \( \xi_\epsilon(\tau_\xi) \equiv \xi_{\parallel,\perp} \), in full agreement with the above relation between \( \tau_\xi \) and \( \xi \).

It is intriguing that MCT predicts near the A3 point a logarithmic behaviour for both the correlation function and for the dynamical correlation length, \( \xi \sim \ln^2 t \). This corresponds to the so-called Sinai diffusion law, which governs the dynamics of domain walls in the RFIM along the branches of a tree. As noted above, the logarithmic behaviour turns into a power law behaviour \( \xi \sim t^{\alpha/2} \) in the presence of a field, with a continuously varying exponent, exactly as for the Sinai model. Whether this analogy is accidental or reveals a deep and interesting physical feature of the MCT formalism remains to be seen.