We derive an extension of the mode coupling theory for the liquid-glass transition to a class of models of confined fluids, where the fluid particles evolve in a disordered array of interaction sites. We find that the corresponding equations are similar to those describing the bulk, implying that the methods of investigation which were developed there are directly transferable to this new domain of application. We then compute the dynamical phase diagram of a simple model system and show that new and nontrivial transition scenarios, including reentrant glass transitions and higher-order singularities, can be predicted from the proposed theory.

Since the mode coupling theory (MCT) of the liquid-glass transition was proposed in the mid-eighties \[1,2\], it has acquired a central role in this field of research \[3,4,5\]. Indeed, on the experimental or numerical side, it is very often to the predictions of the MCT that new data are first confronted \[4,5\], and on the theoretical side, models of increasing complexity are regularly investigated within the MCT framework as a means to unveil potential new phenomena \[6\].

The reason for this strong influence of the MCT lies in its ability to reproduce important phenomenological aspects of the dynamics of supercooled liquids: First, of course, the slowing down of the structural relaxation when density is increased or temperature decreased, but other more specific features as well, like the two-step relaxation scenario. Moreover, it makes a number of precise universal predictions especially suitable for comparisons with experiment or simulation results, and, for simple enough systems for which the MCT is tractable as a first principle theory, it provides detailed predictions concerning nonuniversal aspects of the dynamics as well, allowing thus extensive quantitative tests of the theory \[4,5\].

In the past few years, a rapidly growing interest for the dynamics of liquids under confinement has built into the glass transition community \[7\], with the aim of clarifying the concept of cooperativity, a key ingredient of many glass transition theories \[8\]. Indeed, confinement has appeared as a means to impose to a glassforming system a new characteristic lengthscale (pore size, film thickness...), which should interact with any correlation or cooperativity developing in it, possibly leading to indirect informations on the nature and evolution with temperature of cooperativity. In the course of these investigations, at least for some systems studied by computer simulation \[9,10,11\], many features of the dynamics of bulk glassforming liquids which had found an interpretation in the framework of the MCT have been uncovered. It then appeared natural to compare the corresponding data with the predictions of the MCT, even if the theory had been designed for bulk fluids, and, because the tests were quite successful, the idea emerged that a mode coupling scenario was at work in confined fluids as well.

It seems thus that there is a clear need for an extension of the MCT to confined glassforming liquids. First, if this theory turned out to be similar enough to the theory for the bulk, this would put the studies of simulation data mentioned above on firmer grounds, and more generally this would provide a framework for the analysis of experimental or numerical data on confined fluids. Second, and maybe more importantly, by applying the new theory to various models, as it was done with its bulk counterpart, a thorough exploration of the phenomenology of confined glassforming systems would become possible, potentially allowing to disentangle the different physical effects which interplay in these systems.

It is the aim of this Letter to provide such an extension of the MCT for a particular class of confined systems, the so-called “quenched-annealed” (QA) binary mixtures. In these systems, first introduced by Madden and Glandt \[12\], the fluid molecules equilibrate in a matrix of particles frozen in a disordered configuration sampled from a given probability distribution. The models studied in Refs. \[10,13,14\] belong to this class of systems, as does the Lorentz model, which corresponds to a zero fluid density limit. Besides the proposed theory will borrow ideas from the mode coupling approaches to the diffusion-localization transition in this model \[15,16,17\].

The theory is derived using the projection operator method described in Ref. \[14\]. In the present problem, the inner product of two arbitrary dynamical variables \(A\) and \(B\) is given by \(〈AB^*〉\), where \(\ast\) denotes complex conjugation, \(〈· · · 〉\) a thermal average taken for a given realization of the matrix and \(\cdots \) a subsequent average over the matrix realizations. We thus consider a fluid made of \(N_f\) particles of mass \(m\), adsorbed in a homogeneous disordered matrix consisting of \(N_m\) immobile sites. The system has volume \(V\), hence the fluid and matrix densities are respectively \(n_f = N_f/V\) and \(n_m = N_m/V\). As in the bulk MCT, the dynamical variables of interest are the Fourier components of the microscopic fluid density, \(ρ_f(q,t) = \sum_{j=1}^{N_f} e^{iq\cdot r_j(t)}\), where \(q\) denotes the wavevector and \(r_j(t)\) is the position of the fluid particle \(j\) at time \(t\). But, before proceeding with the dynamical theory, one has to take care of certain peculiarities of the
statics of QA systems. Indeed, because of the presence of the quenched component, for a given matrix realization, the translational invariance of the system is broken. This implies that, at variance with bulk fluids, time-dependent density fluctuations exist at equilibrium, i.e., \( \langle \rho^2 \rangle \neq 0 \). This fact is well known from the derivation, using the replica method, of the Ornstein-Zernike (OZ) equations describing this type of systems [13, 14, 20], where it leads to the splitting of the total and direct correlation functions of the fluid, respectively \( h^f(r) \) and \( c^f(r) \), into two contributions, connected \( [h^c(r) \text{ and } c^c(r)] \) and blocked or disconnected \( [h^b(r) \text{ and } c^b(r)] \). A similar splitting occurs for the structure factor of the fluid \( S_q^{ff} = \langle \rho_q \rho_q \rangle / N_f \) with \( N_f = 1 + n_f h_q^{ff} \), leading to \( S_q^{ff} = S_q^c + S_q^b \) with \( S_q^c = \langle (\rho_q - \langle \rho_q \rangle) (\rho_q - \langle \rho_q \rangle) \rangle / N_f + 1 + n_f h_q^c \) and \( S_q^b = \langle \rho_q \rangle \langle \rho_q \rangle / N_f = n_f h_q^b \), where \( f_q \) denotes the Fourier transform of \( f(r) \). For future reference, we define the matrix-matrix and fluid-matrix structure factors and total correlation functions as well, which are given by \( S_q^{mm} = \langle \rho_q \rho_m \rangle / N_m = 1 + n_m h_q^{mm} \) and \( S_q^{fm} = \langle \rho_q \rho_f \rangle / \sqrt{N_f N_m} = \sqrt{N_f N_m} h_q^{fm} \) ; \( \rho_q^c = \sum_{j=1}^N e^{i q s_j} \), where \( s_j \) is the fixed position of the matrix particle \( j \), is the \( q \) Fourier component of the quenched microscopic matrix density.

It thus follows that, if one is only interested in the relaxing part of the fluid density fluctuations, one has to consider the dynamical variable \( \delta \rho_q^f(t) = \rho_q^f(t) - \langle \rho_q \rangle \) rather than \( \rho_q^f(t) \) itself. Using the standard method, a generalized Langevin equation for the time evolution of the normalized autocorrelation function of the connected density fluctuations \( \phi_q(t) = \langle \delta \rho_q^f(t) \delta \rho_q^f / \langle N_f S_q^c \rangle \rangle \) can then be derived, which is formally identical to the equation for bulk fluids, i.e.,

\[
\dot{\phi}_q + \Omega_q^2 \phi_q + \Omega_q^2 \int_0^t d\tau M_q(t - \tau) \phi_q(\tau) = 0,
\]

with \( \Omega_q^2 = q^2 k_B T / (m S_q^c) \), where \( T \) is the temperature and \( k_B \) the Boltzmann constant. The memory function is given by \( \Omega_q^2 M_q(t) = \langle R_q(t) R_q(t) / \langle N_f m k_B T \rangle \rangle \) where \( R_q(t) = \exp[i(1 - \mathcal{P}) \mathcal{L}(1 - \mathcal{P}) t] \mid i(1 - \mathcal{P}) \mathcal{L} \rho_q \rangle = \) the projected random force obtained from the longitudinal fluid momentum density fluctuation \( \rho_q^f(t) \) \( \mathcal{L} \) is the Liouville operator of the system and \( \mathcal{P} \) is the projector onto the subspace of dynamical variables spanned by \( \delta \rho_q^f \) and \( \rho_q^f \).

We now obtain the slow decaying portion of the memory kernel with a mode coupling approach, assuming that the slow decay of the projected random force autocorrelation function is dominated by couplings to two types of quadratic dynamical variables, \( E_q^{(1)} = \delta \rho_q^f \delta \rho_q^f \) in analogy with the bulk MCT, and \( E_q^{(2)} = \delta \rho_q^f \rho_q^m \), following previous work on the Lorentz gas [13, 14, 17]. Defining the projector \( \mathcal{P} \) on the subspace spanned by the \( B_{q,k} \)'s, the mode coupling part of the memory function is then expressed as \( \Omega_q^2 M_q^{(MC)}(t) = \langle \mathcal{P} R_q(t) \mathcal{P} R_q(t) \rangle / \langle N_f m k_B T \rangle \rangle \) To complete the calculation of \( M_q^{(MC)} \), two steps remain. First, a factorization approximation is required to express four-point density correlations into products of two-point density correlations. Following the usual mode coupling prescription then leads to (we note \( \mathcal{Z} = 1 - \mathcal{P} \))

\[
\langle e^{i \mathcal{Z} \mathcal{P} \mathcal{T}} \delta \rho_q^f \delta \rho_q^f \rangle \simeq (\delta \rho_q^f)^2 N_f S_q^c S_q^c \phi_q \phi_q(t) \phi_q(t) \phi_q(t),
\]

\[
\langle e^{i \mathcal{Z} \mathcal{P} \mathcal{T}} \delta \rho_q^f \delta \rho_q^m \rangle \simeq \delta \rho_q^f N_f S_q^c S_q^m \phi_q(t) \phi_q(t),
\]

\[
\langle e^{i \mathcal{Z} \mathcal{P} \mathcal{T}} \delta \rho_q^m \delta \rho_q^m \rangle \simeq 0.
\]

A crucial point here is that, since the matrix is quenched, \( \rho_q^m \) shows no thermal fluctuations: \( \langle \delta \rho_q^m(t) \delta \rho_q^m \rangle \) is thus identically zero [remember that \( \delta \rho_q^m(t) = \rho_q^m(t) - \langle \rho_q^m \rangle \)]

Second, one needs to calculate \( \langle R_q B_q^{(1)} \rangle = (\mathcal{Z} \mathcal{P} \mathcal{L} B_q^{(1)} - (\mathcal{Z} \mathcal{P} \mathcal{L} B_q^{(1)})) \), the first term is readily handled by application of the Yvon theorem, just as in the bulk MCT. The second one is far more delicate, since it involves three-point connected static correlations of the QA system. Usually, such terms are estimated using the so-called convolution approximation [21] which leads to remarkable simplifications in the resulting mode coupling equations. An extension of the convolution approximation to QA systems has thus been developed which gives

\[
\langle \delta \rho_q^f \delta \rho_q^f \delta \rho_q^f \rangle = N_f S_q^c S_q^c S_q^c,
\]

\[
\langle \delta \rho_q^f \delta \rho_q^f \delta \rho_q^m \rangle = \sqrt{N_f N_m S_q^c S_q^c S_q^m}.
\]

Eventually, assuming that the contributions to the memory kernel not included in \( M_q^{(MC)} \) can be replaced by a white noise term \( \Gamma_q \delta(t) \), we obtain the mode coupling equations for the collective dynamics of a QA mixture, Eq. 11
FIG. 1: Dynamical phase diagram of a hard sphere fluid confined in a matrix of identical hard spheres frozen in an equilibrium configuration. $\phi_f$ and $\phi_m$ denote respectively the fluid and matrix compacities. Point E is the common endpoint of the type A and type B transition lines.

with $M_q(t) = \Gamma_q \delta(t) + M^{(MC)}_q(t)$ and

$$M^{(MC)}_q(t) = \frac{1}{V} \sum_k V^{(2)}_{q,k} \phi_k(t) \phi_{q-k}(t) + V^{(1)}_{q,k} \phi_k(t),$$

$$V^{(2)}_{q,k} = \frac{1}{2} n_f S^c_q \left[ \frac{q \cdot k}{q^2} c^c_k + \frac{q \cdot (q-k)}{q^2} c^c_{q-k} \right] \gamma^2 S^c_{k|q-k}|q-k|^2,$$

$$V^{(1)}_{q,k} = n_m S^c_q \left[ \frac{q \cdot (q-k)}{q^2} c^c_k + n_f \frac{q \cdot k}{q^2} c^c_{q-k} \right] \gamma^2 \left( \frac{h_f^{m}}{S^c_{|q-k|}} \right)^2 S^c_{k|q-k}|q-k|^2,$$

where the replica OZ equations were used to introduce the relevant direct correlation functions [18, 19].

The same procedure can be applied to the dynamics of a tagged particle and the corresponding equations will be reported in a forthcoming paper.

Equations (1) and (2) form the proposed MCT for QA mixtures. Like in the bulk, they involve static quantities only, and, more crucially, they retain the mathematical structure of the typical mode coupling equations which have been extensively studied in Ref. [3]. Thus, all the known properties of the solutions of MCT equations, in particular their universal behaviors, apply \textit{a priori} unchanged to QA mixtures. This means that, in principle, the analysis performed in Ref. [10] is as legitimate as all the analogous ones done on bulk systems.

As one would expect, the present theory integrates the previously known mode coupling theories as limiting cases: In the limit of vanishing matrix density, the bulk MCT [2] is recovered, while in the limit of vanishing fluid density, the MCT equations for the Lorentz gas [17] are obtained. Since both limits show ergodicity-breaking transitions (ideal glass transitions in the first case, diffusion-localization transitions in the second), the present theory, which “interpolates” between them, is bound to display such phenomena.

To illustrate this point and as a first demonstration of the potentialities of the theory, we have computed the dynamical phase diagram of a simple QA system (the models of Refs. [10, 13] would be quite complex for a preliminary study). This is the one studied in Ref. [14], which consists of a fluid of hard spheres confined in a matrix of hard spheres frozen in an equilibrium configuration. Both the fluid and matrix particles have diameter $\sigma$, and the system is characterized by two volume fractions $\phi_f = \pi n_f \sigma^3/6$ and $\phi_m = \pi n_m \sigma^3/6$. The Percus-Yevick approximation [18, 22] is used to compute the required structural quantities. Since we are confronted to basically the same equations as in bulk systems, the numerical procedures to track ergodicity-breaking transitions signalled by the appearance of a nonzero infinite time limit to $\phi_q(t)$ do not differ from those used there. We have applied the method which is described in Ref. [23].

The corresponding dynamical phase diagram is reported in Fig. 1. It consists of two transition lines. On the one hand, starting from the bulk fluid ($\phi_m = 0$) transition point and increasing $\phi_m$, one follows a line of discontinuous
or type B transitions, where \( f_q = \lim_{t \to \infty} \phi_q(t) \) jumps discontinuously from zero to a nonzero value when moving from the ergodic liquid phase to the nonergodic glassy phase. Along this line, as \( \phi_m \) is increased, the amplitude of the jump decreases to zero and the exponent parameter \( \lambda \), which determines many properties of the solutions of the mode coupling equations \( \lambda^\prime, \lambda^\prime, \lambda^\prime \), increases from its bulk value (of about .73) to one, its largest allowed value. On the other hand, moving away from the diffusion-localization (\( \phi_f = 0 \)) transition point by increasing \( \phi_f \), one follows a line of continuous or type A transitions, from which \( f_q \) grows continuously from zero when the system enters in the glassy domain. Here, as \( \phi_f \) is increased, \( \lambda \) grows continuously from zero to one, the allowed interval for type A transitions.

Both lines connect smoothly at a common endpoint E, where \( \lambda = 1 \) for both. Point E corresponds to a degenerate A\(_3\) singularity, a generic type of topologically stable singularities already known from the so-called F\(_{12}\) model \[24\]. To our knowledge, this widely studied one equation toy model had never found any physical realization until now. This result has important physical implications, since, in the vicinity of such a higher-order singularity, the dynamics are known to display very specific features, most significantly logarithmic decay laws and subdiffusive behaviors \[3, 4, 25\].

Beside this specific bifurcation scenario, and formally not related to it, another remarkable prediction of the present theory lies in the shape of the phase diagram. Indeed, starting from the zero fluid density limit and increasing \( \phi_f \), the matrix density at which the system becomes frozen first increases, reaches a maximum and then decreases until the bulk limit is reached. The last behavior can be easily understood from simple free volume arguments: Because of the volume excluded by the matrix particles, the larger the matrix density is, the smaller the fluid density has to be for structural arrest to occur. The first regime however is quite unexpected and might be due to a partial relaxation of the dynamical correlations which lead to the localization of a single particle moving in the porous medium by the introduction of collective density fluctuations at a finite but small fluid density. Overall, this nonmonotonic behavior of \( \phi_m \) at the dynamical transition leads to reentrant type A transitions, i.e., for a given matrix density, ergodicity can be broken both by an increase or a decrease of the fluid density.

All these predictions (bifurcation scenario, logarithmic decay laws, shape of the transition lines, evolutions of \( f_q \) and \( \lambda \) along these lines) can be tested by computer simulations to judge of the validity of the present theory. Unfortunately, the focus of the work of Ref. \[14\] was not on a putative mode coupling scenario and thus only indirect and not so convincing comparisons in favor of the theory can be made. For instance, these authors found that at the lowest investigated fluid density (\( \phi_f = 0.05 \)), the dependence of the diffusion coefficient on \( \phi_m \) was different from the one found at higher fluid densities. This might be a signature of the nonmonotonicity of the transition line in this low fluid density regime. Another of their observations, made in Ref. \[13\] as well and not so surprising, is that the inclusion of matrix particles slows down the dynamics more efficiently than the inclusion of the same amount of fluid particles. Here, this is reflected in the fact that the total compacity \( \phi_{tot} = \phi_f + \phi_m \) at the transition is a decreasing function of \( \phi_m \) in the top part of the phase diagram of Fig. 4. Thus, at a transition point, the corresponding value of \( \phi_{tot} \) being held fixed, an increase of \( \phi_f \) at the expense of \( \phi_m \) leads to an ergodic system, while the reverse change drives the system deeper into the nonergodic domain. This looks encouraging, but clearly more simulation work is needed.

In summary, we have developed an extension of the MCT to the QA mixture model of confined fluids. The corresponding equations turn out to be similar to those of the MCT for the bulk, so that all the applications of the theory which have been conceivable for the bulk, like tests of its universal predictions or quantitative comparisons with computer simulations for simple models, are transposable to the present class of systems. The calculation of the dynamical phase diagram of a simple system shows that new and complex bifurcation scenarios can be predicted and that a rich phenomenology could be unveiled by a systematic study of models of increasing complexity. Such a work is under way.

This of course does not exhaust the question of a general mode coupling description of confined glassforming fluids. Indeed, the QA mixture has the simplifying feature that it corresponds to a statistically homogeneous confinement, while many studies have been done for slit, cylindrical or spherical geometries of the confining medium. The present development should nevertheless represent a valuable means to improve our general understanding of the slow dynamics of confined glassforming liquids.

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