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Field theoretic formulation of a mode-coupling equation for colloids

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The only available quantitative description of the slowing down of the dynamics upon approaching the glass transition has been, so far, the mode-coupling theory, developed in the 80's by Götze and collaborators. The standard derivation of this theory does not result from a systematic expansion. We present a field theoretic formulation that arrives at very similar mode-coupling equation but which is based on a variational principle and on a controlled expansion in a small dimensionless parameter. Our approach applies to such physical systems as colloids interacting via a mildly repulsive potential. It can in principle, with moderate efforts, be extended to higher orders and to multipoint correlation functions.

When a suspension of polymer particles is cooled or compressed, a rapid slowing down of the dynamics occurs, and the suspension gradually becomes solid on experimental time scales, without any apparent change in structure [1]. This phenomenon is called the colloidal glass transition, and it is reminiscent of the phenomenology of molecular glasses. However colloids are conceptually simpler to analyze: the interaction potential often has a simple repulsive character (instead of a Lennard-Jones form) and their effective dynamics is Brownian (instead of Newtonian). They are also experimentally simpler to probe, since colloids are much larger ($\sim 1 \mu\text{m}$) than molecules in simple liquids. An important class of colloids are those who interact via a bounded, repulsive potential. These colloids, due to the existence of a finite energy scale in the potential, exhibit a re-entrant behaviour at high density –the glass melts upon increasing the density– and the non-interacting liquid is recovered in the limit of infinite density [2–4]. In such colloids, all particles evolve in a thermal bath (the solution) and thus undergo individual Brownian motions, while also interacting via a given pair-potential v . To make our approach explicit, we chose to study the harmonic spheres model, where the pair-potential v is taken to be of the form: $v(r) = \varepsilon \left(1 - \frac{r}{\sigma}\right)^2 \theta\left(1 - \frac{r}{\sigma}\right)$, but most of the reasoning will be carried out for an arbitrary, sufficiently well-behaved function v . This model was introduced by Durian [5] in the context of foam mechanics, where $v(r)$ plays the role of an effective interaction potential that arises from a coarse-graining procedure, but experimental realizations in colloids [6, 7] exist, and it became a model system to study glassy structure and dynamics [8].

The position $\vec{r}_i(t)$ of each of the N particles composing the colloidal suspension evolve under Brownian dynamics, encoded in the following Langevin equations:

$$\frac{d\vec{r}_i}{dt}(t) = - \sum_{j \neq i} \vec{\nabla}_{\vec{r}_i} v(\vec{r}_i(t) - \vec{r}_j(t)) + \vec{\xi}_i(t), \quad (1)$$

$$\left\langle \xi_i^\alpha(t) \xi_j^\beta(t') \right\rangle = 2T \delta_{ij} \delta_{\alpha\beta} \delta(t - t'), \quad (2)$$

where T is the temperature of the bath, ξ_i^α is a Gaus-

sian white noise, i, j are particle indices and α, β are space direction indices. It is our goal to obtain quantitative predictions for the dynamics of the dense liquid phase of such colloidal suspensions upon approaching the glass transition; this is a very difficult task which is the subject of active research. And in fact the only successful first-principles theory to this day is the Mode-Coupling Theory (MCT) developed by Götze and collaborators [9, 10]. This is a closed, self-consistent equation of evolution for the relaxation of density fluctuations in equilibrium supercooled liquids. This theory was initially applied to particles evolving under Hamiltonian dynamics, but was later extended by Szamel and Löwen [11] to the physically relevant case of interacting Brownian particles. No significant difference between these descriptions [12] emerges, at least within the MCT approximation. In both frameworks MCT predicts a strict dynamical arrest, so that below a critical temperature, density fluctuations are prevented from relaxing at long times, and ergodicity is spontaneously broken. While successes and failures of MCT are now well documented [13], a systematic way of improving this approximation scheme to overcome the listed pitfalls is still lacking, since the original kinetic formulation of MCT involves physically motivated, but mathematically ill controlled approximations bearing on high-order correlation functions, and it contains no *a priori* small parameter.

The purpose of this letter is to present a new derivation of an MCT equation that bypasses several known pitfalls at the same time: non-interacting particles ($v = 0$) are exactly dealt with. In our work, there exists a small dimensionless parameter, the strength of the potential ε/T . It follows from a well defined variational principle. It can in principle easily be extrapolated to higher-orders, and finally calculations for four-point quantities as well as for sheared systems can easily be implemented.

In order to gain insight into what could be a second order MCT, the idea of formulating MCT in a field theoretic formulation is a very appealing one, since one can then make contact with the toolbox of diagrammatic expansions *à la* Feynman and standard ap-

proximations developed in hard condensed matter and particle physics. Several crucial steps have been made over the past ten years in this direction. Preliminary works [13, 14] have soon been shown to be inconsistent with micro-reversibility, a property which is neither automatically conserved by standard approximations in field theory. Since MCT predicts an ergodic-nonergodic transition, it is crucial to ensure that this transition to a non-ergodic phase does not result from a symmetry breaking approximation. Further attempts [15–17] have considerably progressed into the conservation of micro-reversibility, but technical difficulties led to either a non closed equation for density correlations, or to non physical behavior of the solutions to the equations.

In recent years, Kawasaki and Kim [18] obtained a result consistent with reversibility, and which led to the same equation as that of the original MCT, but this result stems from a very cumbersome calculation, giving little hope of extending this result to higher orders. In the present letter, we suggest to further exploit the many-body theory tools used in condensed matter, by formally treating our classical particles as bosons. We will see that this approach automatically solves several of the problems encountered in previous attempts of the formulation of a field-theoretic MCT, and provides a transparent way to carry the approximations to next order, or to extend the calculation to different quantities, such as four-point correlators, or to non equilibrium settings, such as in sheared systems. We now proceed with a step-by-step presentation of our approach.

The N coupled Langevin equations Eq. (2) can be described by a Fokker-Planck equation governing the evolution of the probability $P(\{\vec{r}_i\}, t)$ of finding each particle i at a given position \vec{r}_i at a time t . As a consequence of micro-reversibility, the Fokker-Planck equation converges towards a Gibbsian equilibrium distribution $P(\{\vec{r}_i\}, t \rightarrow \infty) = e^{-U(\{\vec{r}_i\})/T}$, $U = \sum_{i < j} v(\vec{r}_i - \vec{r}_j)$ being the total potential energy of the system. A standard result [19] shows that the knowledge of the equilibrium distribution allows one to symmetrize the Fokker-Planck operator, making it Hermitian in the proper basis (this is often called the Darboux or supersymmetry transformation). Hermiticity allows one to interpret this new Fokker-Planck equation as a quantum mechanical problem for interacting bosons. From there we use standard methods of quantum field theory [20] to describe the dynamics of the system, which is encoded in the following action:

$$S[a, \bar{a}] = \int_{t, \vec{x}} \left[\bar{a} \partial_t a + \vec{\nabla} \bar{a} \cdot \vec{\nabla} a \right] + V_{\text{eff}}[\bar{a}a]/T. \quad (3)$$

which is expressed in terms of a pair of complex and conjugate fields \bar{a} and a . The kinetic term reflects the free diffusion of particles, and the two-body interactions with potential v are expressed, in the quantum formulation, by the effective potential that now contains not only two

but also three-body interactions as follows:

$$V_{\text{eff}}[\rho] = \frac{1}{4T} \int_{t, \vec{x}, \vec{y}, \vec{z}} \rho(\vec{x}) \vec{\nabla}_{\vec{y}} v(\vec{x} - \vec{y}) \rho(\vec{y}) \cdot \vec{\nabla}_{\vec{z}} v(\vec{x} - \vec{z}) \rho(\vec{z}) - \frac{1}{2} \int_{t, \vec{x}, \vec{y}} \rho(\vec{x}) \Delta_{\vec{x}} v(\vec{x} - \vec{y}) \rho(\vec{y}), \quad (4)$$

where $\rho = \bar{a}a$ is the physical density and v is the pair potential between the colloids.

It is important to notice that the symmetrization corresponds to a change of basis, so that this field theory does not represent directly the physical problem anymore. It was shown long ago [21, 22] that the micro-reversibility of usual dynamical field-theories obtained from the regular Fokker-Planck equation is represented by a complicated, non linear transformation, making it very difficult to preserve when performing mode-coupling approximations [16]. In the symmetrized theory, micro-reversibility is simply encoded in the hermiticity of the symmetrized operator, which is a symmetry property that is very easy to check and conserve even when performing approximations. Furthermore, setting the pair-potential to 0 cancels the effective potential in Eq. (4) and one recovers, without approximation, the free diffusion of colloids. Furthermore, even if the dynamics described by the action Eq. (3) is only related to the real dynamics by a change of basis, careful analysis of the theory shows that far from initial and final conditions (in the “bulk” of the time window), the difference between the modified dynamics and the real dynamics vanishes. Finally, keeping in mind that the pair potential $v(r)$ has an energy scale ε , we see that this approach gives a satisfactory basis for a perturbation expansion in powers of the potential, i.e. in powers of ε/T . Our approach yields a theory that is expressed with ladder operators a and \bar{a} that do not directly represent the physical density $\rho = \bar{a}a$. Introducing it by hand via a Lagrange multiplier (a ghost field) λ , we arrive at a field theory involving four independent fields. To conclude the layout for the diagrammatic expansion to come, we prefer working with fields defined by deviations around the saddle of the action, which describe a homogeneous and isotropic liquid state of mean density ρ_0 . Thus we set $\rho(\vec{x}, t) = \rho_0 + \delta\rho(\vec{x}, t)$, and obtain:

$$Z = \int \mathcal{D}\phi \exp(-S_0[\phi] - \Delta S[\phi]), \quad (5)$$

$$S_0[\phi] = \frac{1}{2} \int d\omega dk \phi(-k, -\omega) G_0^{-1}(k, \omega) \phi(k, \omega), \quad (6)$$

$$\Delta S[\phi] = \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} \gamma \text{---} \text{---} \text{---}, \quad (7)$$

$$G_0^{-1}(k, \omega) = \begin{pmatrix} 0 & i\omega + k^2 & -\sqrt{\rho_0} & 0 \\ -i\omega + k^2 & 0 & -\sqrt{\rho_0} & 0 \\ -\sqrt{\rho_0} & -\sqrt{\rho_0} & 0 & 1 \\ 0 & 0 & 1 & u(k) \end{pmatrix}, \quad (8)$$

$$u(k) = \frac{k^2}{2\rho_0} \left[\left(1 + \frac{\rho_0 v(k)}{T} \right)^2 - 1 \right], \quad (9)$$

$$\gamma(k_1, k_2, k_3) = \frac{1}{2T^2} [k_1 \cdot k_2 v(k_1)v(k_2) + \text{perms.}]. \quad (10)$$

In our diagrammatic representation (7), a straight line stands for the fluctuations of a , an arrowed line stands for the fluctuations of \bar{a} , a dashed line stands for λ the Lagrange multiplier and a wiggly line stands for the density fluctuations field $\delta\rho$. We now turn to the procedure allowing us to determine the correlations of our fields.

The physical quantity that we are ultimately interested in is the matrix element of the two point correlator of the theory G that describes density-density correlations. Since our theory contains four fields, G is a 4 by 4 matrix, with 10 independent entries. Our goal is to obtain a closed equation bearing on the $\delta\rho$ - $\delta\rho$ element only. Performing a double Legendre transform of the dynamical partition function, one obtains a functional of the correlator G , called the 2PI or the Luttinger-Ward functional, $\Phi[G]$. A careful analysis of this functional, which can be found in modern field theory and condensed matter textbooks [23, 24], shows that it has several remarkable properties. First it provides a variational principle to obtain the correlator G : the functional attains its maximum when evaluated at the true correlator. It provides an easy way to compute the inverse of the correlator, since it is obtained as the functional derivative of $\Phi[G]$ with respect to G . Diagrammatically, it is composed of all two particle irreducible diagrams (2PI), allowing for simple truncations of the complete expression of Φ : one can for example decide to retain only the simpler diagram, or try to resum a certain subclass of diagrams. Finally, any truncation of Φ can be shown to preserve the symmetries included in the action, in our case we use this property to conserve micro-reversibility when performing approximations. To obtain a self-consistent approximation for the two point correlator, one constructs an approximation for the Luttinger-Ward functional by selecting a certain subclass of diagrams that contribute to it. In our theory one must construct all 2PI diagrams from the vertices drawn in Eq. (7). For example, the two simplest diagrams that contribute have the following topology:

$$\Phi[G] = \begin{array}{c} \text{---} \circ \text{---} \\ \text{---} \circ \text{---} \end{array} + \begin{array}{c} \text{---} \circ \text{---} \\ \text{---} \circ \text{---} \\ \text{---} \circ \text{---} \end{array} + \dots \quad (11)$$

Then an expression for the vertex function Σ (the inverse of the correlator) is obtained by functionally differentiat-

ing with respect to G :

$$\Sigma[G] = \begin{array}{c} \text{---} \circ \text{---} \\ \text{---} \circ \text{---} \end{array} + \begin{array}{c} \text{---} \circ \text{---} \\ \text{---} \circ \text{---} \\ \text{---} \circ \text{---} \end{array} + \dots \quad (12)$$

Finally, a self consistent equation is obtained by exploiting the inverse relationship that exists between Σ and G (sometimes referred to as the Schwinger-Dyson equation):

$$(G_0^{-1} - \Sigma[G]) G = 1 \quad (13)$$

This variational approach can be seen as the dynamical counterpart to the density functional theory of liquids: one constructs a diagrammatic expression for the grand potential that involves the unknown correlation function. A truncation of this expression is performed, and an approximation for the direct correlation function (the static counterpart of Σ) is obtained by differentiation of this truncation. Finally this approximation is inserted into the Ornstein-Zernike equation (static counterpart to the Schwinger-Dyson equation) to yield a closed, self consistent equation for the correlation function. Very successful approximations like the hyper-netted chain or the Percus-Yevick approximations of liquid theory have, in the past, been derived in this way [25].

So far, all these considerations are in principle exact. In the following we present the simplest self-consistent approximation that can be obtained within this formalism, and we will see that we obtain an equation that has the exact same structure as that of the Mode-Coupling equation. We can now exploit the fact that our theory contains a small parameter, namely the strength of the potential, to select the lowest order beyond mean-field. We have two vertices in the theory, one that is of order 4 in ε , and one that is of order 0. We want to stay to the lowest non-trivial order, so we can neglect the former.

We only retain the simplest diagram in the expression of the Luttinger-Ward functional Eq. (11), and will justify this *a posteriori*. We obtain an expression for the vertex function in the following form:

$$\Sigma[G](\vec{k}, \tau) = \int_{\vec{q}} \Gamma(\vec{k}, \vec{q}) G(\vec{k} - \vec{q}, \tau) G(\vec{q}), \quad (14)$$

where Γ is a vertex than must be calculated from Eq. (7). Insertion into the Schwinger-Dyson equation then yields

$$G_0^{-1} G(\vec{k}, \tau) = \int_{t', \vec{q}} \Gamma(\vec{k}, \vec{q}) G(\vec{k} - \vec{q}, \tau - t') G(\vec{q}, \tau - t') G(\vec{k}, t') \quad (15)$$

This equation must be understood in the matrix sense, so that, *a priori*, all correlators appear. Note that (15) in itself already has the structure of the mode-coupling equation, in which the memory kernel is itself a quadratic functional of the correlators, except that it applies to

a matrix instead of a scalar. In order to write down an equation that involves only the density-density correlator, we must express all other correlators in terms of $C(\vec{k}, t - t') = \langle \delta\rho(-\vec{k}, t')\delta\rho(\vec{k}, t) \rangle$. At the mean-field level, all correlators are proportional, and we use these proportionality relations and insert them into Eq. (15). The proportionality coefficients involve various powers of ε/T , and one can then verify that, when inserting the proportionality relations into the expression of the Luttinger-Ward functional, all contributions coming from the diagrams that we neglected are indeed of higher order in ε/T .

In Eq.(11) only the topology of the diagrams is represented, but one has to draw all possible diagrams from the vertices of the theory. Even for the simplest watermelon diagram, this involves 11 independent diagrams. Fortunately, to lowest order (order 2 in ε/T) only one diagram is involved, and the final evolution equation for C is:

$$0 = -\partial_\tau^2 C(\vec{k}, \tau) + \Omega(k)^2 C(\vec{k}, \tau) \quad (16)$$

$$+ \frac{1}{2\rho_0} \int_{t', \vec{q}} \mathcal{M}(\vec{k}, \vec{q}) C(\vec{q}, \tau - t') C(\vec{k} - \vec{q}, \tau - t') \partial_{t'} C(\vec{k}, t'),$$

where the memory kernel has the following expression:

$$\mathcal{M}(\vec{k}, \vec{q}) = \left[\vec{q}^2 c(\vec{q}) + (\vec{k} - \vec{q})^2 c(\vec{k} - \vec{q}) \right]^2 \quad (17)$$

Note that, as usual in field theoretic formulations, one has to resort to a further approximation, i.e. setting $c(\vec{k}) = -v(\vec{k})/T$. This results from the treatment on equal footing of the statics and the dynamics by the approximation we made. The statics of equation (17) is closely similar to the original mode-coupling equation, apart from the slightly different wave-vector dependence that the original mode-coupling approach predicts, in which the factors \vec{q}^2 and $(\vec{k} - \vec{q})^2$ in the rhs of (17) are replaced with $\vec{k} \cdot \vec{q}$ and $\vec{k} \cdot (\vec{k} - \vec{q})$, respectively. Focusing on the long-time behaviour of this equation, and assuming that the density density correlation function does not decay to zero, one makes the usual ansatz: $\lim_{t \rightarrow \infty} C(\vec{k}, t) = \rho_0 S(\vec{k}) f(\vec{k})$, and seek an equation for the non-ergodicity parameter $f(\vec{k})$. By Laplace transform methods one easily obtains:

$$\frac{f(k)}{1 - f(k)} = \frac{\rho_0 S(k)}{8\pi^2 k^4} \int_{\vec{q}} \mathcal{M}(\vec{k}, \vec{q}) S(\vec{q}) S(\vec{k} - \vec{q}) f(\vec{q}) f(\vec{k} - \vec{q}) \quad (18)$$

One can then numerically solve this equation with an iterative procedure. The inputs are $c(k)$ and $S(k)$ for the equilibrium liquid, than can be calculated within the Hyper-Netted Chain approximation for example. Exactly as in the case of standard MCT, one finds that there exists a transition line $T_{MCT}(\rho)$ above which $f(k) = 0$ is the only solution, whereas below $T_{MCT}(\rho)$, a nonzero $f(k)$ is found, i.e. ergodicity is spontaneously broken.

A posteriori, we are inclined to view the MCT equation as a high-temperature expansion. In Fig. 1 we show the resulting $f(k)$ at packing fraction 0.53 and temperature 10^{-4} . The qualitative behavior is very similar, ex-

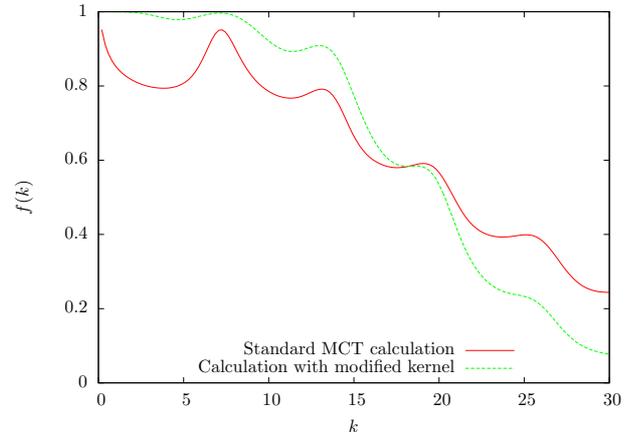


FIG. 1: Non-ergodicity parameter $f(k)$ calculated with the regular MCT kernel (full line) and within our modified kernel (dotted line), at packing fraction 0.53 and temperature 10^{-4} .

cept for the limit $k \rightarrow 0$, where Eq. (18)) is found to give $f(k) \underset{k \rightarrow 0}{\sim} 1$. The modification of the kernel implies that the absolute value of the transition temperature is slightly modified. For example at the packing fraction 0.53, the regular MCT transition, as calculated in [26] is located approximately at $T_{MCT} \approx 10^{-4}$, whereas our rough numerical estimate is $T_{MCT} \approx 8 \cdot 10^{-4}$.

In this letter we have presented a comprehensive approach to write down mode-coupling equations based on a variational principle. In the example of bounded interactions, we have shown that when the strength of the interaction is taken as an expansion parameter, it is possible to write down, to lowest-order, a mode-coupling equation that is similar to the regular MCT equation. We believe that the present strategy can be extended in a variety of directions. The most obvious one is retaining higher orders in the expansion parameter ε/T . The resulting equation for the 7-dimensional order parameter G will pick up a G^5 contribution to its memory kernel. Retaining, after appropriate substitutions based on the leading order expansion (15), the next order in ε/T seems a tedious yet quite accessible task. But it would also be of interest to examine whether qualitative differences show up if the full set of ten equations (15) were solved. Among the self-consistency check of our approach, we mention that the Bethe-Salpeter equation for the four point correlation function could allow us to work without the density field and its conjugate Lagrange multiplier. Beyond the previous technical matters, on our to-do list we also have more pressing wishes. One of them is to implement the so-called "thermodynamic of histories" formalism [27, 28] and to probe the relationships between

ergodicity breaking and dynamic phase transitions. The fate of ergodicity breaking and dynamic phase transitions under shear also belongs to our open questions.

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