

## Mode-coupling theory for heteropolymers

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We study the Langevin dynamics of a heteropolymer by means of a mode-coupling approximation scheme, giving rise to a set of coupled integro-differential equations relating the response and correlation functions. The analysis shows that there is a regime at low temperature characterized by out-of-equilibrium dynamics, with violation of time-translational invariance and of the fluctuation-dissipation theorem. The onset of aging dynamics at low temperatures gives insight into the nature of the slow dynamics of a disordered polymer. We also introduce a renormalization-group treatment of our mode-coupling equations, which supports our analysis, and might be applicable to other systems.

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### I. INTRODUCTION

The dynamics of a heteropolymer chain is relevant for the problem of protein folding and also from a fundamental point of view. Since a protein is composed of monomers of different chemical natures, it is important to understand the effect of heterogeneity on the kinetics of a polymer chain. Such results might give insight into the possible folding pathways of proteins or longer chains. Although the influence of quenched or annealed disorder on the thermodynamics of polymers is a largely investigated area of study [1], together with the effect of random fields [2], random charges along the chain (polyelectrolytes and polyampholytes) [3], in solution or at the interface between two fluids [4], little is known about dynamics.

Previous studies concerning the statics of heteropolymers show that there exists a frozen phase at low temperature, very similar to a spin-glass phase [5], which is a nonergodic state characterized by a very slow relaxation. Recent phenomenological and analytical developments have reproduced the experimental evidence of aging in spin-glasses [6]. Below a certain temperature, the system relaxes in a slower and slower way as the waiting time—which is the time elapsed between the beginning of the experiment and the observation time—is increased; the dependence on the waiting time is clearly proved experimentally in spin-glasses and in other glasses [7,8]. The relaxation follows a power law and both time-translational invariance and the fluctuation dissipation theorem are violated. Similar properties have been found theoretically for the study of large-time out of equilibrium dynamics of a manifold in a random potential [9]. These results are of great interest for systems where disorder or frustration are present, and similar ideas start to be applied, for instance, for the rheology of soft glassy materials [10], or for the dynamics of structural glasses, where experimental evidence of the violation of the fluctuation-dissipation theorem has recently been reported [11].

Concerning the dynamics of heteropolymers, few studies exist at present [12,13] and some of them show that there may be some glassy behavior as the temperature is lowered [14], or that the relaxation should follow a stretched exponential law [15]. There is indeed numerical evidence of stretched exponential relaxation for randomly branched poly-

mers [16], or for the reptation of polymers in disordered media [17], as well as experimental evidence of the same phenomenon for glasses and proteins [18]. Moreover, there is a growing literature about the dynamics of homogeneous but strongly frustrated polymer systems, such as polymer melts where stretched-exponential laws are observed through computer simulations [19], and with dynamics very similar to the one observed in structural glasses or supercooled liquids [20]. Other approaches to the problem of dynamics of heteropolymers in melts use the concept of reptation to compute in a phenomenological way the relaxation time of a disordered chain [21]. Finally, another type of interesting system that could be of interest for the dynamics of proteins can be found in [22], where a spin system with both quenched randomness and ferromagnetic ordering interactions is studied.

Our work concerns the study of the Langevin dynamics of a heteropolymer, treated in the mode-coupling approximation (MCA) scheme. Our motivation for using this approximation is based on several previous studies that led to significant results. This procedure goes beyond perturbation theory (though not in a very controlled way) and is therefore useful when one wants to study strong-coupling effects. The scheme is to expand the microscopic quantities involved in the Langevin equation to lowest nontrivial order in the potential—as if it was a perturbation procedure—and then to replace in the correction terms the bare correlation functions (those corresponding to the problem without potential) by the full correlation functions one wants to compute. This amounts to resumming a certain class of diagrams and hence to go further than the weak-coupling regime. This type of procedure has been used by Kraichnan in the context of turbulence as a way to find the Kolmogorov laws starting from the Navier-Stokes equation [23]; it has also been used for the KPZ equation where exponents close to those found by dynamic renormalization group were computed [24]. Interestingly, it has also been found that the MCA is exact for some special models with quenched disorder whose dynamics can be studied exactly in a mean-field approach, using functional methods; this is true in particular for the  $p$ -spin spherical spin-glass model [25]. So one can hope that the MCA approach is able to capture dynamic effects such as aging that arise from the presence of disorder in a nonperturbative way.

Finally, it has been pointed out that the general coupled set of equations obtained through MCA looks very much like those found in the context of the mode-coupling theory introduced by Gotze [20], which gives a reliable description of the slow dynamics of supercooled liquids, reinforcing the link between glassy systems which are frustrated, but contain no disorder, and disordered systems such as spin-glasses.

In the following, we show that the same approximation (MCA) can be used for the dynamics of a disordered polymer and that out-of-equilibrium features can be found as well. These results may be of relevance for heteropolymer melts, or for very long chains of heteropolymers. From a protein-oriented point of view, such results may not be directly applicable, since they are derived for an infinite and purely random system. However, for large proteins, one may observe some intermediate slow regime of folding in the globular state, between the fast initial hydrophobic collapse, and the final relaxation towards the native state once a nucleus [26] has been formed.

## II. THE MODE-COUPLING APPROACH

### A. Formal developments

We introduce here a model of heteropolymer dynamics and explain how to derive a set of coupled integro-differential equations using the mode coupling approximation. We use a standard Hamiltonian for a disordered polymer, where a quenched potential  $V(s, \vec{\phi}(s, t))$  is applied and comes from the random nature of the interactions between monomers. In our notations,  $\vec{\phi}(s, t)$  is the position of monomer  $s$  at time  $t$ ,  $s$  being the coordinate of the monomer along the chain,  $s = 1, \dots, N$ .  $d$  is the dimensionality of the space and  $a_0$  is the Kuhn length,

$$\mathcal{H} = \frac{1}{2a_0^2} \int ds \sum_{\alpha=1}^d \left( \frac{\partial \phi_\alpha}{\partial s} \right)^2 + \int ds V(s, \vec{\phi}(s, t)). \quad (1)$$

More explicitly, the random potential is

$$\begin{aligned} V(s, \vec{\phi}(s, t)) &= \int ds' B(s, s') \delta(\vec{\phi}(s, t) - \vec{\phi}(s', t)) \\ &= \int ds' B(s, s') \int \frac{d\vec{q}}{(2\pi)^d} \\ &\quad \times \exp i \sum_{\alpha} q_{\alpha} [\phi_{\alpha}(s, t) - \phi_{\alpha}(s', t)]. \quad (2) \end{aligned}$$

We use a bar to perform the average over the disorder, and we assume that the value of the interaction between too different monomers is distributed in a Gaussian way.

$$\overline{B(s, s')} = 0,$$

$$\overline{B(s_1, s'_1) B(s_2, s'_2)} = B_0^2 \delta(s_1 - s_2) \delta(s'_1 - s'_2).$$

We consider the Langevin equation for such a polymer:

$$\begin{aligned} \left[ \frac{\partial}{\partial t} - \frac{1}{a_0^2} \frac{\partial^2}{\partial s^2} \right] \phi_{\alpha}(s, t) &= - \frac{\partial}{\partial \phi_{\alpha}(s, t)} \int ds V(s, \vec{\phi}(s, t)) \\ &\quad + \eta_{\alpha}(s, t), \quad (3) \end{aligned}$$

with a Gaussian thermal noise  $\vec{\eta}(s, t)$ ,

$$\langle \eta_{\alpha}(s, t) \rangle = 0,$$

$$\langle \eta_{\alpha}(s, t) \eta_{\beta}(s', t') \rangle = 2T \delta(s - s') \delta(t - t') \delta_{\alpha\beta}.$$

Our aim is to compute correlation and response functions, or at least know their qualitative behavior with time. Following earlier studies, we do not assume *a priori* time-translational invariance and we define respectively the correlation function and the response function as quantities depending on two distinct times,  $t$  and  $t'$ :

$$C(s, t; s', t') = \frac{1}{d} \sum_{\alpha=1}^d \overline{\langle \phi_{\alpha}(s, t) \phi_{\alpha}(s', t') \rangle}, \quad (4)$$

$$\begin{aligned} G(s, t; s', t') &= \frac{1}{d} \sum_{\alpha=1}^d \overline{\left\langle \frac{\partial \phi_{\alpha}(s, t)}{\partial \eta_{\alpha}(s', t')} \right\rangle} \\ &= \frac{1}{d} \frac{1}{2T} \sum_{\alpha=1}^d \overline{\langle \phi_{\alpha}(s, t) \eta_{\alpha}(s', t') \rangle}. \quad (5) \end{aligned}$$

The last identity holds as long as the random noise  $\vec{\eta}(s, t)$  is Gaussian.

During all this study, we shall use Fourier transforms, which we define, both for the position  $\vec{\phi}(s, t)$  and for the correlation functions, with  $\omega_n = 2\pi n/N$ ,

$$\vec{\phi}_{\alpha}^n(t) = \frac{1}{N} \int_0^N e^{i\omega_n s} \phi_{\alpha}(s, t) ds,$$

$$\vec{G}^n(t, t') = \frac{1}{N} \int_0^N e^{i\omega_n (s' - s)} G(s, t; s', t') ds ds'.$$

The same type of definition applies for  $\vec{\eta}_{\alpha}^n(t)$  and  $\vec{C}^n(t, t')$ .

The standard procedure in the MCA is first to find the solution  $\vec{\phi}_{\alpha}^n(t)$  of the Langevin equation, up to the first non-zero order in perturbation. The dynamic equation can be rewritten in Fourier space:

$$\frac{\partial \vec{\phi}_{\alpha}^n(t)}{\partial t} = - \frac{\omega_n^2}{a_0^2} \vec{\phi}_{\alpha}^n(t) - \lambda \vec{W}_{\alpha}^n(t) + \vec{\eta}_{\alpha}^n(t), \quad (6)$$

where we have added for convenience the coefficient  $\lambda$  as the perturbative parameter;  $\lambda$  is eventually set back to 1 at the end of the expansion. And the quantity  $\vec{W}_{\alpha}^n(t)$  is defined as

$$\begin{aligned} \tilde{W}_\alpha^n(t) &= \frac{2}{N} \int_0^N e^{i\omega_n s} ds \int_0^N ds' B(s, s') \int \frac{d\vec{q}}{(2\pi)^d} i q_\alpha \\ &\times \exp i \sum_\alpha q_\alpha (\phi_\alpha(s, t) - \phi_\alpha(s', t)), \end{aligned} \quad (7)$$

If  $\lambda$  is equal to 0 we are reduced to the ‘‘bare’’ problem of an elastic chain in a harmonic potential. Then the Langevin equation is exactly solvable and the solution is

$$\tilde{\Phi}_{\alpha,0}^n(t) = \int_0^t dt' \tilde{G}_0^n(t, t') \tilde{\eta}_\alpha^n(t'), \quad (8)$$

where  $\tilde{G}_0^n(t, t')$  is the  $n$ th Fourier component of the bare response function, and

$$\tilde{G}_0^n(t, t') = e^{-(\omega_n^2 a_0^2)(t-t')} \theta(t-t'). \quad (9)$$

In the following we shall set  $a_0 = 1$ .

When one now adds the disorder-dependent term  $\tilde{W}_\alpha^n(t)$  in the Langevin equation, then

$$\tilde{\Phi}_\alpha^n(t) = \int_0^t dt' \tilde{G}_0^n(t, t') [\tilde{\eta}_\alpha^n(t') - \lambda \tilde{W}_\alpha^n(t')] \quad (10)$$

is the exact solution, which actually gives an implicit equation for the quantity  $\tilde{\Phi}_\alpha^n(t)$  that cannot be solved in a straightforward way.

Note that we have assumed here for the initial condition that  $\tilde{\Phi}_\alpha^n(0) = 0$ . This corresponds to a very extreme configuration where the polymer is completely collapsed. This is also the most practical choice as far as the complexity of the calculation is concerned. Although it is an extreme case, we think that the dynamics in the collapsed phase will still be well described (and this will be discussed in more detail in the last section of this paper). One could also have chosen random initial conditions, which should not change the final long-time results, as was shown, for example, in similar problems of spin-glass dynamics [27,28], and also in a study of a disordered polymer [12].

One then performs in this expression an expansion up to second order in  $\lambda$ , and we refer the reader to Appendix A for more details. It is then rather straightforward, though computationally lengthy, to compute  $\tilde{G}^n(t, t')$  and  $\tilde{C}^n(t, t')$  as functions of the bare quantities such as  $\tilde{G}_0^n(t, t')$  and  $\tilde{C}_0^n(t, t')$ , which are at the end replaced by the full or ‘‘renormalized’’ quantities  $\tilde{G}^n(t, t')$  and  $\tilde{C}^n(t, t')$ . One finally ends up with a set of coupled equations which solutions will, in principle, fully describe the dynamics of the original system. We can write these equations in a compact way:

$$\begin{aligned} \left[ \frac{\partial}{\partial t} + \omega_n^2 \right] \tilde{G}^n(t, t') &= \delta(t-t') + \int_0^t dt_1 R_n(t, t_1) \tilde{G}^n(t, t') \\ &+ \int_{t'}^t dt_1 \Sigma_n(t, t_1) \tilde{G}^n(t_1, t'), \end{aligned} \quad (11)$$

$$\begin{aligned} \left[ \frac{\partial}{\partial t} + \omega_n^2 \right] \tilde{C}^n(t, t') &= \int_0^t dt_1 R_n(t, t_1) \tilde{C}^n(t, t') \\ &+ \int_0^{t'} dt_1 D_n(t, t_1) \tilde{G}^n(t', t_1) \\ &+ \int_0^{t'} dt_1 \Sigma_n(t, t_1) \tilde{C}^n(t_1, t'). \end{aligned} \quad (12)$$

All quantities  $R_n(t_1, t_2)$ ,  $\Sigma_n(t_1, t_2)$ ,  $D_n(t_1, t_2)$  involved in the coupled set of equations are defined in Appendix A, and depend only on  $\tilde{G}^p(t, t')$  and  $\tilde{C}^p(t, t')$ , with  $p \neq 0$ . This set of dynamical equations is rather typical of the mode-coupling approximation, and similar sets of coupled equations have been already encountered, for example, in [9,24,27]. They can either be solved numerically or require additional assumptions to get more information on the solutions.

## B. Analysis of the equations

A very difficult task is to solve the set of integro-differential equations described above. One major difficulty lies on the fact that all modes are coupled, and as it has already been observed for example for the mode-coupling equations of the KPZ model [24,29], the numerical treatment for these equations presents numerous problems. We have not been able to make significant progress in that direction; not only should it require a recursive algorithm with careful check for the convergence of all functions, but we also expect some divergences in the long time regime, which would require the introduction of unknown cutoffs.

In our analysis, we took into account all terms found in the former section, without truncating them with too crude approximations. However, it would be interesting in the future to find a way to simplify these equations (even if the connection with the initial model becomes then less obvious), that would reproduce the results that we find here.

The first step in the analysis can be done by focusing on the large time limit and looking for an ansatz for the correlation functions in that time domain. Let us assume that one can write, in the limit where  $t \rightarrow \infty$  and  $t' \rightarrow \infty$ , with  $t' \ll t$ ,

$$\tilde{C}^n(t, t') = q f_n \left( \frac{t'}{t} \right)^\gamma, \quad (13)$$

$$\tilde{G}^n(t, t') = \frac{q'}{t} f_n \left( \frac{t'}{t} \right)^{\gamma-1}. \quad (14)$$

Such an ansatz also contains a generalized version of the fluctuation-dissipation theorem (FDT) (this has already been introduced in earlier studies [27]), which can be written

$$\tilde{G}^n(t, t') = x \frac{\partial}{\partial t'} \tilde{C}^n(t, t'), \quad (15)$$

where  $x$  is the coefficient  $x = q' / \gamma q$ .

We want to plug this ansatz (13) and (14) into the mode-coupling equations, and see whether this is an acceptable

solution. This is done in detail in Appendix B for any temperature  $T$ . Let us explain briefly here how the algebra works.

After replacing into the mode-coupling equations, one is left with implicit equations for  $q$ ,  $f_n$ ,  $x$ , and  $\gamma$ , but the dependence on time cancels out in the limit of large times. This is what makes the ansatz consistent, at least as far as the dependence on time is concerned. We give computational details in Appendix B. In particular, in the equation for  $\tilde{C}^n(t, t')$ ,  $D_n(t_1, t_2)$  can be written as a sum of four contributions  $D_n^{(i)}(t_1, t_2)$ ,  $i=0,1,2,3$  as shown in Appendix A. The terms involving  $D_n^{(2)}(t_1, t_2)$  and  $D_n^{(3)}(t_1, t_2)$  are shown to be negligible in the limit of large times, and also if the temperature is not too large: this makes the time cancellation possible. All parameters  $q$ ,  $f_n$ ,  $x$ , and  $\gamma$  have a dependence on temperature, which is hard to find analytically. The remaining equations on  $q$ ,  $f_n$ ,  $x$ , and  $\gamma$  are too difficult to solve numerically, since they require the introduction of cutoffs—see Appendix B—to stop the divergences in the integrals when the two time arguments become too close to each other [in particular, both  $\tilde{G}^n(t, t')$  and  $\tilde{C}^n(t, t')$  have different analytical forms when  $t' \rightarrow t$ , which we do not know].

The two extreme cases  $T=0$  and  $T=\infty$  can be looked at more closely in this problem, even if we have shown that the above ansatz is an acceptable solution at large times for any temperature  $T$  small enough. In the case where  $T=0$ , the equations can be simplified more, the terms involving  $D_n^{(2)}(t_1, t_2)$  and  $D_n^{(3)}(t_1, t_2)$  are actually equal to zero and one sees easily that the above ansatz still remains valid, for the same reasons as the ones explained above (see Appendix B). We were also able to show that a time-translational solution was not acceptable, by taking some appropriate trial functions such as exponentials or stretched exponentials. We give details on this point in Appendix B also.

If we study the limit  $T \rightarrow \infty$ , one is left with a single term in the equation for  $\tilde{C}^n(t, t')$ :

$$\int_0^{t'} dt_1 D_n^{(3)}(t, t_1) \tilde{G}^n(t', t_1) = 0. \quad (16)$$

The power-law ansatz used above can no longer satisfy this condition.

However, if one assumes time-translational invariance and the usual fluctuation-dissipation theorem ( $G(\tau) = [-\theta(\tau)/T] \partial_\tau C(\tau)$ ) the mode-coupling equations are simply satisfied. In the limit of infinite temperature, one is actually left with the simple Rouse model for a homopolymer chain, and an exponential time relaxation.

Such information about a glassy behavior at low temperatures with power-law behavior leads naturally to think of the existence of a critical temperature  $T_c$  that may separate the glassy, non-FDT, nontime translational invariant regime from a high temperature regime where the relaxation would be typically exponential. Although it is not possible to determine this temperature from our equations, it should be easier to observe such a phenomenon in simpler models of polymers, or by studying numerical models of polymers.

### III. AN ALTERNATIVE TREATMENT OF THE MODE-COUPLING EQUATIONS: FUNCTIONAL RENORMALIZATION GROUP APPROACH

In view of the difficulties raised by the mode-coupling equations, one has to search for new analytical methods to try and solve them. One of them is to apply a functional renormalization group analysis to the mode-coupling equations themselves. To our knowledge, such a method has never been used in this context. For the present problem, this procedure enables us to have more information about the analytical form of the correlation functions. In particular, it can justify some scaling form for their analytical expressions, as soon as one finds a fixed point in the RG procedure that is believed to represent the small frequency, small wave-vector regime. This is motivated by the fact that we are mostly interested in the long times limit, and in the long-distance regime ( $s - s' \rightarrow \infty$ , along the chain).

In the case of the disordered polymer, our dynamic RG calculation gives rise to a fixed point. However, the fixed points equations are themselves hard to solve. We also believe that such a method could be of interest for simpler and largely studied systems, such as the KPZ equation, but we did not look at this case here.

In this type of calculation [30], we want to integrate out the fast wave-vector modes and keep only the slow modes, the ones with small wave vectors. One should also, in principle, do the same thing for high frequencies, to keep track only of the low frequency part; this can be done by expressing all the quantities in frequency space, but we did not describe this part here for simplicity. In order to integrate out the fast wave-vector modes, we first switch from discrete to continuous Fourier variables, by replacing  $\sum_n$  by  $\int d^D k / (2\pi)^D$  with an upper cutoff  $\Lambda$ , where  $D$  is the dimension of the chain (in our case,  $D=1$ ). The wave vectors such that  $\Lambda/b < |\vec{k}| < \Lambda$  can be integrated out in all quantities, where  $b = e^{\delta l}$  is close to 1 ( $\delta l \rightarrow 0$ ); then the only perturbative parameter here is  $\delta l$ . After integration, we denote the quantities  $Q$  for which the  $|\vec{k}|$  integration is now only  $\int_0^{\Lambda/b} d^D k / (2\pi)^D$ , by  $Q^<$ .

In order to harmonize the notations with the ones in the preceding section, we now note  $\tilde{G}^k(t, t')$  and  $\tilde{C}^k(t, t')$  the  $k$ th Fourier component of the correlation functions, and still use the notation  $D_k$ ,  $R_k$ ,  $\Sigma_k$  for the mode-coupling kernels.

In a more convenient way than the ones used in the previous section, the starting mode-coupling equations we used can be rewritten in the form originally derived in Appendix A (see also [25]):

$$\begin{aligned} \tilde{C}^k(t, t') &= \tilde{C}_0^k(t, t') \\ &+ \int_0^t dt_1 \int_0^{t'} dt_2 \tilde{G}^k(t, t_1) D_k(t_1, t_2) \tilde{G}^k(t', t_2), \end{aligned} \quad (17)$$

$$\begin{aligned} \tilde{G}^k(t, t') &= \tilde{G}_0^k(t, t') + \int_0^t dt_1 \tilde{G}_0^k(t, t_1) \\ &\times \left[ \int_0^{t_1} dt_2 R_k(t_1, t_2) \tilde{G}^k(t_1, t') \right. \\ &\left. + \int_0^{t_1} dt_2 \Sigma_k(t_1, t_2) \tilde{G}^k(t_2, t') \right]. \end{aligned} \quad (18)$$

In such a way, we can write for a quantity  $\tilde{Q}^k(t_1, t_2)$ , the following one-order expansion in  $\delta l$  ( $Q = G, C, R, \Sigma, D$ ):

$$\tilde{Q}^k(t_1, t_2) = \tilde{Q}^{k<}(t_1, t_2) - \delta l Q_k(t_1, t_2). \quad (19)$$

The corrections  $Q_k(t_1, t_2)$  can be computed and only involve the different quantities  $G_0$  and  $Q^{<}$ . We give more details on this computation in Appendix C. In particular, for  $\mathcal{G}_k(t, t')$  and  $C_k(t, t')$ , we have

$$\begin{aligned} \mathcal{G}_k(t, t') &= \int_0^t dt_1 \tilde{G}_0^k(t, t_1) \left[ \int_0^{t_1} dt_2 \mathcal{R}_k(t_1, t_2) \tilde{G}^k(t_1, t') \right. \\ &+ \int_0^{t_1} dt_2 \mathcal{S}_k(t_1, t_2) \tilde{G}^k(t_2, t') \\ &+ \int_0^{t_1} dt_2 R_k(t_1, t_2) \mathcal{G}_k(t_1, t') \\ &\left. + \int_0^{t_1} dt_2 \Sigma_k(t_1, t_2) \mathcal{G}_k(t_2, t') \right], \end{aligned} \quad (20)$$

$$\begin{aligned} C_k(t, t') &= \int_0^t dt_1 \int_0^{t'} dt_2 [\tilde{G}^k(t, t_1) D_k(t_1, t_2) \mathcal{G}_k(t', t_2) \\ &+ \tilde{G}^k(t, t_1) \mathcal{D}_k(t_1, t_2) \tilde{G}^k(t', t_2) \\ &+ \mathcal{G}_k(t, t_1) D_k(t_1, t_2) \tilde{G}^k(t', t_2)]. \end{aligned} \quad (21)$$

The next step is to do a rescaling of all quantities and write a differential equation for the renormalization flow where the increment is  $\delta l$ . One has then to make scaling assumptions, which are expected, at least at the fixed points, if any. Then, if one assumes

$$\tilde{Q}^k(t, t') = \frac{1}{k^\chi} q(tk^z, t'k^z), \quad (22)$$

where  $z$  is the dynamic exponent, the renormalized quantity is

$$\tilde{Q}_k^R(t, t') = b^{-\chi} \tilde{Q}^{(bk)^<}(b^{-z}t, b^{-z}t'). \quad (23)$$

By expanding this last expression to first order in  $\delta l$  one finally ends up with

$$\frac{\partial \tilde{Q}^k}{\partial l} = -\chi \tilde{Q}^k(t, t') + k \frac{\partial \tilde{Q}^k}{\partial k} - zt \frac{\partial \tilde{Q}^k}{\partial t} - zt' \frac{\partial \tilde{Q}^k}{\partial t'} + Q_k(t, t'). \quad (24)$$

More specifically, we assumed the following scaling forms, which are compatible with the mode-coupling equations:

$$\tilde{C}^k(t, t') = \frac{1}{k^{2\alpha+D}} c(tk^z, t'k^z), \quad (25)$$

$$\tilde{G}^k(t, t') = \frac{1}{k^{z+D}} g(tk^z, t'k^z), \quad (26)$$

$$D_k(t, t') = \frac{1}{k^{2\alpha-D-4z}} d(tk^z, t'k^z), \quad (27)$$

$$R_k(t, t') = k^{2z} r(tk^z, t'k^z), \quad (28)$$

$$\Sigma_k(t, t') = k^{2z} s(tk^z, t'k^z). \quad (29)$$

We want now to try the ansatz of the previous section [Eqs. (13) and (14)], so we now assume more precisely that

$$\tilde{C}^k(t, t') = \frac{1}{k^{2\alpha+D}} c_1\left(\frac{t'}{t}\right), \quad (30)$$

$$\tilde{G}^k(t, t') = \frac{1}{k^{z+D}} \frac{1}{tk^z} g_1\left(\frac{t'}{t}\right), \quad (31)$$

$$D_k(t, t') = \frac{1}{k^{2\alpha-D-4z}} d_1\left(\frac{t'}{t}\right), \quad (32)$$

$$R_k(t, t') = k^{2z} \frac{1}{tk^z} r_1\left(\frac{t'}{t}\right), \quad (33)$$

$$\Sigma_k(t, t') = k^{2z} \frac{1}{tk^z} s_1\left(\frac{t'}{t}\right). \quad (34)$$

Due to the scaling nature of all quantities, the derivative terms  $\partial \tilde{Q}^k / \partial k$  and  $\partial \tilde{Q}^k / \partial t$  in the flow equations can be simplified and expressed in terms of  $\tilde{Q}^k(t, t')$ , and we end up with the following set:

$$\frac{\partial \tilde{G}^k}{\partial l} = -2(z+D) \tilde{G}^k(t, t') + \mathcal{G}_k(t, t'), \quad (35)$$

$$\frac{\partial \tilde{C}^k}{\partial l} = -2(D+2\alpha) \tilde{C}^k(t, t') + C_k(t, t'), \quad (36)$$

$$\frac{\partial D_k}{\partial l} = -2(2\alpha-D-4z) D_k(t, t') + \mathcal{D}_k(t, t'), \quad (37)$$

$$\frac{\partial R_k}{\partial l} = 4z R_k(t, t') + \mathcal{R}_k(t, t'), \quad (38)$$

$$\frac{\partial \Sigma_k}{\partial l} = 4z \Sigma_k(t, t') + \mathcal{S}_k(t, t'). \quad (39)$$

The fixed points are obtained by setting the  $l$  derivative to 0, and denoting by  $Q^*$  the fixed-point quantities, and replacing in the expressions for  $\mathcal{G}_k(t, t')$  and  $\mathcal{C}_k(t, t')$ , we obtain the self-consistent equations at the fixed point:

$$(z+D)\tilde{G}^{k,*}(t, t') = (D-z) \int_0^t dt_1 \tilde{G}_0^k(t, t_1) \left[ \int_0^{t_1} dt_2 R_k^*(t_1, t_2) \tilde{G}^{k,*}(t_1, t') + \int_0^{t_1} dt_2 \Sigma_k^*(t_1, t_2) \tilde{G}^{k,*}(t_2, t') \right], \quad (40)$$

$$(2\alpha+D)\tilde{C}^{k,*}(t, t') = (2\alpha+D-2z) \int_0^t dt_1 \int_0^{t_1} dt_2 \times \tilde{G}^{k,*}(t, t_1) D_k^*(t_1, t_2) \tilde{G}^{k,*}(t', t_2). \quad (41)$$

We checked that the power-law ansatz used in the first section is still a solution for these equations of fixed point; the procedure of replacing the ansatz in the expressions is exactly the same as the one described in Appendix B. This can then justify its use in the mode-coupling equations (11) and (12) from which we started our analysis, and which represent the real-space quantities of interest; the scaling form of the ansatz is also justified. If we then plug at the fixed point the generalized fluctuation-dissipation theorem  $\tilde{G}^k(t, t') = x(\partial/\partial t') \tilde{C}^k(t, t')$ , we obtain the following relation between exponents:  $\alpha = z$ . Further information on the exponents  $\alpha$  and  $z$  could be obtained by solving numerically coupled equations like Eqs. (40) and (41); this will be done elsewhere.

#### IV. DISCUSSION AND CONCLUSION

The analysis of the mode-coupling equations using renormalization group ideas enabled us to write the dynamic correlation functions of a disordered polymer in terms of scaling functions. Unfortunately, at this point, it does not give much insight into the exact asymptotic time and wave-vector dependence, at large times and large wavelengths. We believe however that this method could be very convenient for more simple examples of stochastic equations, that are treated using mode-coupling techniques.

The main result of the mode-coupling approach is the evidence of the out-of-equilibrium character of the dynamics of heteropolymers, in the thermodynamic limit. The dependence of the dynamic correlation functions on two times—the smaller one being the waiting time—implying no time-translational invariance and a generalized fluctuation-dissipation theorem, is required at low temperatures; more precisely, a power-law dependence on two times is a solution of our set of equations. This contains the aging phenomenon, similar to the one observed in spin-glasses and other types of disordered systems. We expect the aging regime found here to be present as a long transient in finite polymers.

Although we used a very special case of initial conditions in our study, we think that our results still capture the impor-

tant physical properties of the dynamics of a (disordered) polymer in a collapsed state. In particular, if glassiness was not present in such a system, there would be a characteristic time  $\tau$  after which one would finally have time-translational invariance, independently of the chosen initial condition (in particular, even in the case of the initial conditions we chose here). However, we find aging and out-of-equilibrium properties at all time scales; this suggests that our approach still captures this glassy dynamical effect, even in the particular case we considered.

This evidence for glassy behavior was already obtained in a similar study of the dynamics of heteropolymers by Franz *et al.* [12]. Starting from the same Hamiltonian as ours, the dynamics was studied using a supersymmetric formulation of the Martin-Siggia-Rose functional, which was shown by Kurchan [31] to be useful to study the dynamics of systems for which the solution of the statics is known. Their final result is very similar to ours (and they actually start from random initial conditions), and the dynamical equations for the correlation and response functions are of the mode-coupling type [Eqs. (11) and (12)]. Using the results on dynamics of manifolds in a random potential [32], one is then able to predict the aging regime, and a power-law decay of correlation functions, though the precise analytical forms could not be found. These results, obtained with a method relying on the structure of the statics solution of the problem [5], are consistent with ours and the direct dynamical (MCA) approach.

Calculations similar to the one described above in this paper can be made by slightly changing the starting Langevin equation. We replaced the disordered interaction  $B(s, s')$  between monomers by a constant attractive interaction coefficient  $v$ , therefore restricting our study to homopolymers. Remarkably enough, we found that the power-law ansatz still holds at low temperature. The corresponding formulas for the MCA equations are given at the end of Appendix A. The structure of the equations is completely analogous to the disordered case, and we showed that the power-law ansatz is an acceptable solution by following the lines of the calculations of Appendix B. Even in the absence of disorder, the mode-coupling equations seem to induce some apparent disorder in frustrated systems (such as polymer chains in the collapsed phase in this case), and lead to nontrivial glassy behavior. In the MCA approach, it appears that one can capture the frustration character of a collapsed polymeric chain that stems from the competition between the attractive interaction between monomers and the harmonic potential due to the elasticity of the chain [the classical mode coupling theory [20] for glasses also captures frustration in such simple realizations as binary mixtures of Lennard-Jones (LJ) particles].

This similarity of behavior between disordered and non-disordered polymers is not very surprising when one remembers that mode-coupling equations have very similar structures in the disordered and nondisordered version of a given model [25]. More precisely, it has been previously shown that given a nondisordered but frustrated or chaotic model, one can find a disordered model of the same class whose mode-coupling equations are actually exact, and coincide with the approximate mode-coupling equations of the non-disordered model. (This is, however, not exactly the situation

that occurs here, since the mode-coupling closure is only an approximation scheme for our heteropolymer model.) This emphasizes the importance of such studies for real glasses, which are not characterized by the presence of disorder. In particular, our analysis may be helpful to understand the dynamics of polymeric glasses, or melts, that also exhibit aging [8] and vitreous dynamics [19], qualitatively very similar to the physics of binary Lennard-Jones fluid mixtures [33].

It is interesting to note that a great similarity has been observed in the dynamics of supercooled liquids (modeled by binary mixtures LJ particles) and of polymer melts, whereas a few differences are noticeable due to the connectivity effect of the polymeric system [19]. It has been shown that the correlation functions and in particular the dynamic structure factor for polymer melts can be well described by the MCT for liquids. However, the mean-square displacement shows a subdiffusive behavior compared to the case of nonconnected LJ particles, due to the connectivity of the chains. This difference occurs in the  $\alpha$  regime, at large times, that reflects the rearrangements of the chain at scales larger than the size of a particle's cage, whereas the  $\beta$  regime, at small times, corresponds to local movements inside a cage, which are the same in the presence or not of connectivity. On the ground of these microscopic mechanisms, it does not seem surprising either, that a disordered polymer melt or a homogeneous melt may have the same kind of dynamics.

To summarize, our model provides a tentative theoretical framework which allows to exhibit slow dynamics and aging in dense phases of homogeneous or disordered polymers. A further step in this study would be to find an efficient numerical algorithm for the resolution of the mode-coupling equations or of some simplified form of these mode-coupling equations. This would provide the full solutions for the correlation functions, as well as for the mean-square displacement, as functions of time, and allow for a direct comparison with the numerical results of Baschnagel *et al.* [19].

An important issue that also needs to be clarified is in which way the fluctuation-dissipation theorem is violated at long times. It has been shown very recently [34] that in the case of systems with short range interactions, the measurement of the violation of the dissipation-fluctuation ratio is directly related to the pattern of the replica symmetry breaking ("one-step rsb" or "full rsb"). The statics of the heteropolymer model studied here were reported in [5] and showed a one-step replica symmetry breaking, so the fluctuation-dissipation should, according to [34], be of the form given by Eq. (15). In addition, concerning the case of homopolymers, it would be of great interest to use the first principle computations described in [35] and be able to draw a link between the equilibrium and the dynamical properties in the glass phase.

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#### APPENDIX A

In this Appendix, we give the full expressions for the mode-coupling equations obtained in Sec. II, as well as some intermediate results.

Starting from Eq. (10), one performs an expansion to second order in  $\lambda$ , which leads to an approximate expression for  $\tilde{\phi}_\alpha^n(t)$ . This expression is the following:

$$\begin{aligned} \tilde{\phi}_\alpha^n(t) = & \tilde{\phi}_{\alpha,0}^n(t) - \frac{2\lambda}{N} \int_0^t dt' \tilde{G}_0^n(t,t') W_{\alpha,0}^n(t') \\ & + \frac{2\lambda^2}{N} \int_0^t dt' \tilde{G}_0^n(t,t') \int_0^N ds \\ & \times \int_0^N ds' e^{i\omega_n s} B(s,s') \int \frac{d^d q}{(2\pi)^d} i q_\alpha \\ & \times \exp i \sum_\alpha q_\alpha \sum_{m \neq 0} (e^{-i\omega_m s} - e^{-i\omega_m s'}) \tilde{\phi}_{\alpha,0}^m(t') \\ & \times \sum_\beta i q_\beta \sum_{p \neq 0} (e^{-i\omega_p s} - e^{-i\omega_p s'}) \\ & \times \int_0^{t'} dt'' \tilde{G}_0^p(t',t'') W_{\beta,0}^p(t''), \end{aligned}$$

where

$$\begin{aligned} W_{\alpha,0}^n(t') = & \int_0^N ds \int_0^N ds' e^{i\omega_n s} B(s,s') \int \frac{d^d q}{(2\pi)^d} i q_\alpha \\ & \times \exp i \sum_\alpha q_\alpha \sum_{m \neq 0} (e^{-i\omega_m s} - e^{-i\omega_m s'}) \tilde{\phi}_{\alpha,0}^m(t'). \end{aligned}$$

Starting from this expression we calculated  $\tilde{G}^n(t,t')$  and  $\tilde{C}^n(t,t')$ , performing both averages on the random noise and on the disorder. The result can be written in terms of  $\tilde{G}_0^p(t,t')$  and  $\tilde{C}_0^p(t,t')$  only; but the MCA approximation consists in replacing these quantities by the full unknown quantities  $\tilde{G}^p(t,t')$  and  $\tilde{C}^p(t,t')$ , resulting in a set of coupled Dyson equations:

$$\begin{aligned} \tilde{C}_n(t,t') = & \tilde{C}_n^0(t,t') \\ & + \int_0^t dt_1 \int_0^{t'} dt_2 \tilde{G}_n(t,t_1) D_n(t_1,t_2) \tilde{G}_n(t',t_2), \end{aligned}$$

$$\begin{aligned}\tilde{G}_n(t, t') &= \tilde{G}_n^0(t, t') + \int_0^t dt_1 \tilde{G}_n^0(t, t_1) \\ &\times \left[ \int_0^{t_1} dt_2 R_n(t_1, t_2) \tilde{G}_n(t_1, t') \right. \\ &\left. + \int_0^{t_1} dt_2 \Sigma_n(t_1, t_2) \tilde{G}_n(t_2, t') \right].\end{aligned}$$

The mode-coupling equations can be rewritten as integro-differential equations, performing on the left- and right-hand sides of the previous equations a convolution with  $\tilde{G}_n^{0-1}$  (see also [25]). The resulting set of equations is the one introduced in Sec. II:

$$\begin{aligned}\left[ \frac{\partial}{\partial t} + \omega_n^2 \right] \tilde{G}^n(t, t') &= \delta(t - t') + \int_0^t dt_1 R_n(t, t_1) \tilde{G}^n(t, t') \\ &+ \int_0^{t'} \Sigma_n(t, t_1) \tilde{G}^n(t_1, t'),\end{aligned}$$

$$\begin{aligned}\left[ \frac{\partial}{\partial t} + \omega_n^2 \right] \tilde{C}^n(t, t') &= \int_0^t dt_1 R_n(t, t_1) \tilde{C}^n(t, t') \\ &+ \int_0^{t'} dt_1 D_n(t, t_1) \tilde{G}^n(t', t_1) \\ &+ \int_0^t dt_1 \Sigma_n(t, t_1) \tilde{C}^n(t_1, t').\end{aligned}$$

The term  $\int_0^t dt_1 R_n(t, t_1)$  plays the role of a mass and is given by the following expression:

$$\begin{aligned}R_n(t_1, t_2) &= -\frac{2B_0^2}{N^3} \frac{1}{(2\pi)^d} \int_0^N ds_1 \int_0^N ds'_1 (1 - e^{i\omega_n(s'_1 - s_1)}) \\ &\times \sum_{p \neq 0} (1 - e^{i\omega_p(s_1 - s'_1)}) \tilde{G}^p(t_1, t_2)\end{aligned}$$

$$[\Delta(s_1, s'_1; t_1, t_2)]^{-2-d/2} 3X(s_1, s'_1; t_1) Y(s_1, s'_1; t_1, t_2).$$

The quantity  $\Sigma_n(t_1, t_2)$  can be seen as the self-energy associated with the corresponding Dyson equations:

$$\begin{aligned}\Sigma_n(t_1, t_2) &= \frac{2B_0^2}{N^3} \frac{1}{(2\pi)^d} \int_0^N ds_1 \int_0^N ds'_1 (1 - e^{i\omega_n(s'_1 - s_1)}) \\ &\times \sum_{p \neq 0} (1 - e^{i\omega_p(s_1 - s'_1)}) \tilde{G}^p(t_1, t_2) \\ &\times [\Delta(s_1, s'_1; t_1, t_2)]^{-2-d/2} [X(s_1, s'_1; t_1) \\ &\times X(s_1, s'_1; t_2) + 2Y^2(s_1, s'_1; t_1, t_2)].\end{aligned}$$

Finally,  $D_n(t_1, t_2)$  can be seen as a ‘‘renormalized’’ noise correlator, whose expression is reported here:

$$\begin{aligned}D_n(t_1, t_2) &= D_n^{(0)}(t_1, t_2) + D_n^{(1)}(t_1, t_2) + D_n^{(2)}(t_1, t_2) \\ &+ D_n^{(3)}(t_1, t_2).\end{aligned}$$

Each term can be computed separately:

$$D_n^{(0)}(t_1, t_2) = \frac{2T}{N} \delta(t_1 - t_2),$$

$$\begin{aligned}D_n^{(1)}(t_1, t_2) &= \frac{4B_0^2}{N^2} \frac{1}{(2\pi)^d} \int_0^N ds_1 \int_0^N ds'_1 Y(s_1, s'_1; t_1, t_2) \\ &\times [\Delta(s_1, s'_1; t_1, t_2)]^{-1-d/2},\end{aligned}$$

$$\begin{aligned}D_n^{(2)}(t_1, t_2) &= \frac{2B_0^2}{N^2} \frac{2T}{N} \frac{1}{(2\pi)^d} \int_0^N ds_1 \int_0^N ds'_1 (1 - e^{i\omega_n(s'_1 - s_1)}) \\ &\times \sum_{p \neq 0} \int_0^{t_2} dt_3 \tilde{G}^p(t_2, t_3) (1 - e^{i\omega_n(s_1 - s'_1)}) \\ &\times [\Delta(s_1, s'_1; t_1, t_2)]^{-2-d/2} \\ &\times \left( -3X(s_1, s'_1; t_3) Y(s_1, s'_1; t_2, t_3) \right. \\ &\times \int_0^{t_2} dt_4 \delta(t_1 - t_4) \tilde{G}^n(t_2, t_4) \\ &+ [X(s_1, s'_1; t_2) X(s_1, s'_1; t_3) \\ &+ 2Y^2(s_1, s'_1; t_2, t_3)] \\ &\left. \times \int_0^{t_3} dt_4 \delta(t_1 - t_4) \tilde{G}^n(t_3, t_4) \right), \\ D_n^{(3)}(t_1, t_2) &= D_n^{(2)*}(t_2, t_1).\end{aligned}$$

Finally, we used the following notations:

$$X(s_1, s'_1; t_1) = \sum_{m \neq 0} |e^{-i\omega_m s_1} - e^{-i\omega_m s'_1}|^2 \tilde{C}^m(t_1, t_1),$$

$$Y(s_1, s'_1; t_1, t_2) = \sum_{m \neq 0} |e^{-i\omega_m s_1} - e^{-i\omega_m s'_1}|^2 \tilde{C}^m(t_1, t_2),$$

$$\begin{aligned}\Delta(s_1, s'_1; t_1, t_2) &= X(s_1, s'_1; t_1) X(s_1, s'_1; t_2) \\ &- Y^2(s_1, s'_1; t_1, t_2).\end{aligned}$$

Let us now explain briefly what happens in the nondisordered case, where the random variable  $B(s, s')$  is replaced by a constant  $v$ . The corresponding MCA equations have exactly the same structure as in the disordered case [Eqs. (11) and (12)]. The only differences are in the detailed ex



pressions of the kernels, which are more complicated—in the disordered case, some simplifications could occur due to the averaging over disorder, but this is not the case any more if there is no disorder.

The “mass” kernel is

$$R_n(t_1, t_2) = R_n^{(1)}(t_1, t_2) + R_n^{(2)}(t_1, t_2),$$

$$R_n^{(1)}(t_1, t_2) = \frac{2v}{N^2} \delta(t_1, t_2) \int_0^N ds_1 \int_0^N ds'_1 (1 - e^{i\omega_n(s'_1 - s_1)}) \\ \times [X(s_1, s'_1; t_2)]^{-1-d/2},$$

$$R_n^{(2)}(t_1, t_2) = -\frac{2v^2}{N^3} \frac{1}{(2\pi)^d} \int_0^N ds_1 \int_0^N ds'_1 (1 - e^{i\omega_n(s'_1 - s_1)}) \\ \times \sum_{p \neq 0} (e^{-i\omega_p s_1} - e^{-i\omega_p s'_1}) \tilde{G}^p(t_1, t_2) \\ \times \int_0^N ds_2 e^{i\omega_p s_2} \int_0^N ds'_2 \\ \times [W(s_1, s'_1; s_2, s'_2; t_1, t_2)]^{-2-d/2} \\ \times 3X(s_1, s'_1; t_1) Z(s_1, s'_1; s_2, s'_2; t_1, t_2).$$

The “self-energy”  $\Sigma_n(t_1, t_2)$  is given by

$$\Sigma_n(t_1, t_2) = \frac{2v^2}{N^3} \frac{1}{(2\pi)^d} \int_0^N ds_1 e^{-i\omega_n s_1} \int_0^N ds'_1 \sum_{p \neq 0} (e^{-i\omega_p s_1} - e^{-i\omega_p s'_1}) \tilde{G}^p(t_1, t_2) \int_0^N ds_2 e^{i\omega_p s_2} \int_0^N ds'_2 (e^{i\omega_n s_2} - e^{i\omega_n s'_2}) \\ \times [W(s_1, s'_1; s_2, s'_2; t_1, t_2)]^{-2-d/2} [X(s_1, s'_1; t_1) X(s_2, s'_2; t_2) + 2Z^2(s_1, s'_1; s_2, s'_2; t_1, t_2)].$$

Finally, the “renormalized” noise correlator  $D_n(t_1, t_2)$  has the following expression:

$$D_n(t_1, t_2) = \sum_{i=0}^5 D_n^{(i)}(t_1, t_2).$$

Each term can be computed separately:

$$D_n^{(0)}(t_1, t_2) = \frac{2T}{N} \delta(t_1 - t_2),$$

$$D_n^{(1)}(t_1, t_2) = \frac{2v}{N} \frac{2T}{N} \tilde{G}^n(t_2, t_1) \int_0^N ds \int_0^N ds' (1 - e^{i\omega_n(s' - s)}) [X(s, s'; t_2)]^{-1-d/2},$$

$$D_n^{(3)}(t_1, t_2) = \frac{4v^2}{N^2} \frac{1}{(2\pi)^d} \int_0^N ds_1 \int_0^N ds'_1 \int_0^N ds_2 \int_0^N ds'_2 e^{i\omega_n(s_1 - s_2)} Z(s_1, s'_1; s_2, s'_2; t_1, t_2) [W(s_1, s'_1; s_2, s'_2; t_1, t_2)]^{-1-d/2},$$

$$D_n^{(4)}(t_1, t_2) = \frac{2v^2}{N^2} \frac{2T}{N} \frac{1}{(2\pi)^d} \int_0^N ds_1 e^{-i\omega_n s_1} \int_0^N ds'_1 \int_0^N ds_2 \int_0^N ds'_2 \\ \times \sum_{p \neq 0} (e^{i\omega_p(s_2 - s_1)} - e^{i\omega_p(s_2 - s'_1)}) \int_0^{t_2} dt_3 \tilde{G}^p(t_2, t_3) [W(s_1, s'_1; s_2, s'_2; t_1, t_2)]^{-2-d/2} \\ \times \left( -3X(s_1, s'_1; t_2) Z(s_1, s'_1; s_2, s'_2; t_2, t_3) (e^{i\omega_n s_1} - e^{i\omega_n s'_1}) \int_0^{t_2} dt_4 \delta(t_1 - t_4) \tilde{G}^n(t_2, t_4) \right. \\ \left. + [X(s_1, s'_1; t_2) X(s_1, s'_1; t_3) + 2Z^2(s_1, s'_1; s_2, s'_2; t_2, t_3)] (e^{i\omega_n s_2} - e^{i\omega_n s'_2}) \int_0^{t_3} dt_4 \delta(t_1 - t_4) \tilde{G}^n(t_3, t_4) \right),$$

$$D_n^{(2)}(t_1, t_2) = D_n^{(1)*}(t_2, t_1),$$

$$D_n^{(5)}(t_1, t_2) = D_n^{(4)*}(t_2, t_1).$$

Finally, we used the following notations:

$$X(s_1, s'_1; t_1) = \sum_{m \neq 0} |e^{-i\omega_m s_1} - e^{-i\omega_m s'_1}|^2 \tilde{C}^m(t_1, t_1),$$

$$Z(s_1, s'_1; s_2, s'_2; t_1, t_2) = \sum_{m \neq 0} (e^{-i\omega_m s_1} - e^{-i\omega_m s'_1}) \\ \times (e^{-i\omega_m s_2} - e^{-i\omega_m s'_2}) \tilde{C}^m(t_1, t_2),$$

$$W(s_1, s'_1; s_2, s'_2; t_1, t_2) = X(s_1, s'_1; t_1) X(s_2, s'_2; t_2) \\ - Z^2(s_1, s'_1; s_2, s'_2; t_1, t_2).$$

Let us stress here that, thanks to the technical similarities between the MCA equations for the disordered and non-disordered case, the analytical computations developed in Appendix B also apply naturally to the homopolymeric system.

## APPENDIX B

In this appendix, we show how the ansatz proposed by Eqs. (13) and (14) can be a suitable solution for the mode-coupling equations obtained in Sec. II.

We give the expressions of the different terms introduced in Appendix A, after performing adequate change of variables, after the power-law ansatz has been plugged into these terms. Whenever required, we introduced lower and upper cut-offs, assuming that in the extreme regimes of times (short times or  $t' \rightarrow t$ , for which we do not have explicit analytical forms) the integrals are actually convergent, and that the time scaling we find is not modified by these contributions. In all equations we neglect the derivative terms, which is justified in the limit  $t' \ll t$ .

### 1. Equation for $\tilde{G}_n(t, t')$ [see Eq. (11)]

(i) The first term in front of the propagator in the right-hand side of the equation is comparable to a mass:

$$\int_0^t dt_1 R_n(t, t_1) = -\frac{2B_0^2}{N^2} \frac{1}{(2\pi)^d} \\ \times \int_0^N ds (1 - e^{-i\omega_n s}) \frac{3q'}{2q} [X(s)]^{-1-d} \\ \times \int_0^{1-\epsilon} du u^{-1+2\gamma} (1 - u^{2\gamma})^{-2-d/2}.$$

This factor is independent of time, up to the cutoff  $1 - \epsilon$ .

(ii) Concerning the second term, it is in fact proportional to  $\tilde{G}^n(t, t')$ :

$$\int_{t'}^t \Sigma_n(t, t_1) \tilde{G}^n(t_1, t') \\ = \frac{2B_0^2}{N^2} \frac{1}{(2\pi)^d} \int_0^N ds (1 - e^{-i\omega_n s}) \frac{q'^2 f_n}{2q} [X(s)]^{-1-d} \\ \times \int_{t'/t > w}^{1-\epsilon} du u^{-1} (1 - u^{2\gamma})^{-2-d/2} \\ \times [1 + u^{2\gamma}] \frac{1}{t} \left(\frac{t'}{t}\right)^{\gamma-1}.$$

Finally, given the cutoffs  $w$  and  $1 - \epsilon$ , all terms in the equation for  $\tilde{G}^n(t, t')$  are proportional to each other, and hence the dependence on time cancels out.

### 2. Equation for $\tilde{C}_n(t, t')$ [see Eq. (12)]

(i) The first new term that has to be computed is in fact proportional to  $\tilde{C}^n(t, t')$ :

$$\int_{t'}^t \Sigma_n(t, t_1) \tilde{C}^n(t_1, t') \\ = \frac{2B_0^2}{N^2} \frac{1}{(2\pi)^d} \int_0^N ds (1 - e^{-i\omega_n s}) \frac{q' f_n}{2} [X(s)]^{-1-d} \\ \times \int_w^{1-\epsilon} du u^{-1} (1 - u^{2\gamma})^{-2-d/2} [1 + 2u^{2\gamma}] \left(\frac{t'}{t}\right)^{\gamma}.$$

(ii) The remaining terms coming from the  $D_n(t, t_1)$  contribution can be simplified. First, when  $t' < t$ , it is easy to see that the ones involving  $D_n^{(0)}(t, t_1)$  and  $D_n^{(2)}(t, t_1)$  are equally zero.

(iii) The  $D_n^{(1)}(t, t_1)$  contribution is again proportional to  $\tilde{C}^n(t, t')$ ,

$$\int_0^{t'} dt_1 D_n^{(1)}(t, t_1) \tilde{G}^n(t', t_1) \\ = \frac{4B_0^2}{N} \frac{1}{(2\pi)^d} \int_0^N ds q' f_n [X(s)]^{-1-d} \frac{1}{2\gamma} \left(\frac{t'}{t}\right)^{\gamma}.$$

(iv) Finally, the last term has a different time dependence.

$$\int_0^{t'} dt_1 D_n^{(3)}(t, t_1) \tilde{G}^n(t', t_1) \\ = \frac{2B_0^2 T}{N^2} \frac{1}{(2\pi)^d} \int_0^N ds (1 - e^{-i\omega_n s}) \frac{q'}{q} (q' f_n)^2 [X(s)]^{-1-d} \\ \times \left( -3 \int_w^1 du u^{2\gamma-2} \int_0^{1-\epsilon} dv v^{2\gamma-1} [1 - v^{2\gamma}]^{-2-d/2} \right. \\ \left. + \int_w^1 du u^{2\gamma-2} \int_w^{1-\epsilon} dv v^{-1} [1 - v^{2\gamma}]^{-2-d/2} \right) \\ \times \frac{1}{t} \left(\frac{t'}{t}\right)^{\gamma-1}.$$

Because of its scaling behavior in  $t$  and  $t'$ , this term is in fact a subdominant term compared to  $\tilde{C}^n(t, t')$  in the limit  $t \rightarrow \infty$  and  $t' \rightarrow \infty$ ,  $t' \ll t$ . We can neglect it in the limit of large times, and also provided that the temperature  $T$  is not too large. Then all terms in the equation for  $\tilde{C}^n(t, t')$  have the same time dependence, which can then be cancelled.

As was already mentioned in the main text, we tried some other trial functions than the power-law ansatz. In particular, we tried time-translational invariant (TTI) exponential and stretched exponential solutions, following the same algebra as the one described just above. These functions do not work, as they do not lead to a time cancellation of the mode-coupling equations and rather lead to physical contradictions.

Let us show briefly why these solutions are not acceptable. For simplicity we use here stretched or pure exponentials (as they would be the most expected solutions in the case of TTI). Namely, we take, for  $\gamma \leq 1$ ,

$$\tilde{C}^n(t, t') = q_n e^{-f_n(t-t')^\gamma},$$

$$\tilde{G}^n(t, t') = x \frac{\partial}{\partial t'} \tilde{C}^n(t, t') = x q_n \gamma (t-t')^{\gamma-1} e^{-f_n(t-t')^\gamma}.$$

We assume these solutions to be valid for large times, and especially if the time difference  $t-t'$  is small. Let us consider here the integro-differential equation for  $\tilde{G}^n(t, t')$ . In this equation, the first term on the right-hand side,  $\int_0^t dt_1 R_n(t, t_1) \tilde{G}^n(t, t')$  may break TTI. Using the TTI ansatz, we actually find that the time dependence of  $\int_0^t dt_1 R_n(t, t_1)$  is the following:

$$\int_0^t dt_1 R_n(t, t_1) = \int_0^t dt_1 (t-t_1)^{-\gamma(1+d/2)},$$

If  $1 - \gamma(1+d/2) > 0$ , this integral is convergent, and behaves like  $t^{1-\gamma(1+d/2)}$ , which goes to infinity at large times. Consequently, the term  $\int_0^t dt_1 R_n(t, t_1) \tilde{G}^n(t, t')$  violates TTI.

If  $1 - \gamma(1+d/2) < 0$ , the integral is divergent for  $t_1 \rightarrow t$ , and one can see easily that one needs a different behavior of  $\tilde{G}^n(t, t_1)$  in this region of time, which violates TTI. This is a

nonphysical situation as TTI is all the more justified as the time difference is small. So in both cases, the TTI assumption gives contradictory results, which shows that this kind of hypothesis does not hold here.

### APPENDIX C

We present in this appendix a more complete set of results and intermediate computations for the RG approach to the mode-coupling equations presented in Sec. III. We start from Eqs. (17) and (18) that were originally derived at the beginning of Appendix A.

In the expressions for  $D_k, R_k, \Sigma_k$ , as we take the continuous Fourier variable, integrations of the form  $\int_0^\Lambda d^D p / (2\pi)^D$  can be found, where  $\Lambda$  is an upper cutoff. As we want to integrate out large wave-vector modes, we write

$$\begin{aligned} \int_0^\Lambda \frac{d^D p}{(2\pi)^D} A(p) &= \int_0^{\Lambda/b} \frac{d^D p}{(2\pi)^D} A(p) \\ &+ \int_{\Lambda/b}^\Lambda \frac{d^D p}{(2\pi)^D} A(p) \\ &\simeq \int_0^{\Lambda/b} \frac{d^D p}{(2\pi)^D} A(p) + \Lambda \delta l A(\Lambda) \end{aligned}$$

in the limit  $\delta l \rightarrow 0$ , with  $b = e^{\delta l}$ .

We note  $\tilde{Q}^{k <}$  the quantity  $\tilde{Q}$  obtained after integration of the fast modes, where only integrals of the form  $\int_0^{\Lambda/b} d^D p / (2\pi)^D$  remain. This leads to the one-order expansion in  $\delta l$  Eq. (19) of the quantities  $D_k, R_k, \Sigma_k$ . As an example, we give here the expression for  $\mathcal{R}_k(t_1, t_2)$ , but do not mention the other ones as the formulas are quite complicated:

$$\begin{aligned} \mathcal{R}_k(t_1, t_2) &= \frac{2B_0^2}{N^3} \frac{3\Lambda}{(2\pi)^d} \int_0^N ds_1 \int_0^N ds'_1 (1 - e^{ik(s'_1 - s_1)}) [\Delta(s_1, s'_1; t_1, t_2)]^{-2-d/2} \\ &\times \left[ (1 - e^{i\Lambda(s_1 - s'_1)}) \tilde{G}^\Lambda(t_1, t_2) X(s_1, s'_1; t_1) Y(s_1, s'_1; t_1, t_2) + 2\{1 - \cos[\Lambda(s_1 - s'_1)]\} \tilde{C}^\Lambda(t_1, t_1) \right. \\ &\times \int_0^\Lambda dp (1 - e^{ip(s_1 - s'_1)}) \tilde{G}^p(t_1, t_2) Y(s_1, s'_1; t_1, t_2) + 2\{1 - \cos[\Lambda(s_1 - s'_1)]\} \tilde{C}^\Lambda(t_1, t_2) \\ &\times \int_0^\Lambda dp (1 - e^{ip(s_1 - s'_1)}) \tilde{G}^p(t_1, t_2) X(s_1, s'_1; t_1) - 2\left(2 + \frac{d}{2}\right) \frac{\{1 - \cos[\Lambda(s_1 - s'_1)]\}}{\Delta(s_1, s'_1; t_1, t_2)} \\ &\times \int_0^\Lambda dp (1 - e^{ip(s_1 - s'_1)}) \tilde{G}^p(t_1, t_2) X(s_1, s'_1; t_1) Y(s_1, s'_1; t_1, t_2) [X(s_1, s'_1; t_1) \tilde{C}^\Lambda(t_2, t_2) \\ &\left. + X(s_1, s'_1; t_2) \tilde{C}^\Lambda(t_1, t_1) - 2Y(s_1, s'_1; t_1, t_2) \tilde{C}^\Lambda(t_1, t_2) \right], \end{aligned}$$

with

$$X(s_1, s'_1; t_1) = 2 \int_0^\Lambda dp \{1 - \cos[p(s_1 - s'_1)]\} \tilde{C}^p(t_1, t_1),$$

$$Y(s_1, s'_1; t_1, t_2) = 2 \int_0^\Lambda dp \{1 - \cos[p(s_1 - s'_1)]\} \tilde{C}^p(t_1, t_2).$$

Then we used the expansions in  $\delta l$  Eq. (19) of  $R_k, \Sigma_k, D_k$  to find the ones for  $\tilde{G}^k$  and  $\tilde{C}^k$ . This is done by writing the following simple algebra for  $\tilde{G}^k$  and  $\tilde{C}^k$ :

$$\begin{aligned} \tilde{G}^k(t, t') &\simeq \tilde{G}_0^k(t, t') + \int_0^t dt_1 \tilde{G}_0^k(t, t_1) \left[ \int_0^{t_1} dt_2 [R_k^<(t_1, t_2) - \delta l \mathcal{R}_k(t_1, t_2)] [\tilde{G}^{k<}(t_1, t') - \delta l \mathcal{G}_k(t_1, t')] \right. \\ &\quad \left. + \int_0^{t_1} dt_2 [\Sigma_k^<(t_1, t_2) - \delta l \mathcal{S}_k(t_1, t_2)] [\tilde{G}^{k<}(t_2, t') - \delta l \mathcal{G}_k(t_2, t')] \right] \\ &\simeq \tilde{G}^{k<}(t, t') - \delta l \int_0^t dt_1 \tilde{G}_0^k(t, t_1) \left[ \int_0^{t_1} dt_2 \mathcal{R}_k(t_1, t_2) \tilde{G}^k(t_1, t') + \int_0^{t_1} dt_2 \mathcal{S}_k(t_1, t_2) \tilde{G}^k(t_2, t') \right. \\ &\quad \left. + \int_0^{t_1} dt_2 R_k(t_1, t_2) \mathcal{G}_k(t_1, t') + \int_0^{t_1} dt_2 \Sigma_k(t_1, t_2) \mathcal{G}_k(t_2, t') \right], \\ \tilde{C}^k(t, t') &\simeq \tilde{C}_0^k(t, t') + \int_0^t dt_1 \int_0^{t'} dt_2 [ \tilde{G}^{k<}(t, t_1) - \delta l \mathcal{G}_k(t, t_1) ] [ D_k^<(t_1, t_2) - \delta l \mathcal{D}_k(t_1, t_2) ] [ \tilde{G}^k(t', t_2) - \delta l \mathcal{G}_k(t', t_2) ] \\ &\simeq \tilde{C}^{k<}(t, t') - \delta l \int_0^t dt_1 \int_0^{t'} dt_2 [ \tilde{G}^k(t, t_1) D_k(t_1, t_2) \mathcal{G}_k(t', t_2) + \tilde{G}^k(t, t_1) \mathcal{D}_k(t_1, t_2) \tilde{G}^k(t', t_2) \\ &\quad + \mathcal{G}_k(t, t_1) D_k(t_1, t_2) \tilde{G}^k(t', t_2) ], \end{aligned}$$

which gives the following expressions for  $\mathcal{G}_k(t, t')$  and  $\mathcal{C}_k(t, t')$  [Eqs. (20) and (21)]:

$$\begin{aligned} \mathcal{G}_k(t, t') &= \int_0^t dt_1 \tilde{G}_0^k(t, t_1) \left[ \int_0^{t_1} dt_2 \mathcal{R}_k(t_1, t_2) \tilde{G}^k(t_1, t') + \int_0^{t_1} dt_2 \mathcal{S}_k(t_1, t_2) \tilde{G}^k(t_2, t') + \int_0^{t_1} dt_2 R_k(t_1, t_2) \mathcal{G}_k(t_1, t') \right. \\ &\quad \left. + \int_0^{t_1} dt_2 \Sigma_k(t_1, t_2) \mathcal{G}_k(t_2, t') \right], \\ \mathcal{C}_k(t, t') &= \int_0^t dt_1 \int_0^{t'} dt_2 [ \tilde{G}^k(t, t_1) D_k(t_1, t_2) \mathcal{G}_k(t', t_2) + \tilde{G}^k(t, t_1) \mathcal{D}_k(t_1, t_2) \tilde{G}^k(t', t_2) + \mathcal{G}_k(t, t_1) D_k(t_1, t_2) \tilde{G}^k(t', t_2) ]. \end{aligned}$$

We used then an expected scaling form for all functions, as is illustrated in the main text by Eqs. (22) and (25)–(29).

The rescaling step used in the RG procedure is represented by Eq. (23) and can be detailed in the following way for  $\tilde{Q}^k(t, t')$ :

$$\begin{aligned} \tilde{Q}_k^R(t, t') &= b^{-\chi} \tilde{Q}^{(bk)<}(b^{-z}t, b^{-z}t') \\ &\simeq (1 - \delta l \chi) \left[ \tilde{Q}^{k<}(t, t') + \delta l k \frac{\partial \tilde{Q}^{k<}(t, t')}{\partial k} - \delta l z t \frac{\partial \tilde{Q}^{k<}(t, t')}{\partial t} - \delta l z t' \frac{\partial \tilde{Q}^{k<}(t, t')}{\partial t'} \right] \\ &\simeq \tilde{Q}^{k<}(t, t') + \delta l \left[ -\chi \tilde{Q}^{k<}(t, t') + k \frac{\partial \tilde{Q}^{k<}(t, t')}{\partial k} - z t \frac{\partial \tilde{Q}^{k<}(t, t')}{\partial t} - z t' \frac{\partial \tilde{Q}^{k<}(t, t')}{\partial t'} \right] \\ &\simeq \tilde{Q}^k(t, t') + \delta l \left[ \mathcal{Q}_k(t, t') - \chi \tilde{Q}^k(t, t') + k \frac{\partial \tilde{Q}^k(t, t')}{\partial k} - z t \frac{\partial \tilde{Q}^k(t, t')}{\partial t} - z t' \frac{\partial \tilde{Q}^k(t, t')}{\partial t'} \right], \end{aligned}$$

so that taking the limit  $\delta l \rightarrow 0$ , one ends up with the flow equation for  $\tilde{Q}^k(t, t')$ :

$$\frac{\partial \tilde{Q}^k(t, t')}{\partial l} = -\chi \tilde{Q}^k(t, t') + k \frac{\partial \tilde{Q}^k(t, t')}{\partial k} - zt \frac{\partial \tilde{Q}^k(t, t')}{\partial t} - zt' \frac{\partial \tilde{Q}^k(t, t')}{\partial t'} + Q_k(t, t').$$

Using now the fact that for any function with a scaling form of the type:  $X_k(t, t') = (1/k^\beta) f(t'/t)$ , one has

$$k \frac{\partial X}{\partial k} - zt \frac{\partial X}{\partial t} - zt' \frac{\partial X}{\partial t'} = -\beta X,$$

and for  $X_k(t, t') = (1/k^\beta)(1/t) f(t'/t)$ , one has

$$k \frac{\partial X}{\partial k} - zt \frac{\partial X}{\partial t} - zt' \frac{\partial X}{\partial t'} = -(\beta - z)X,$$

we can simplify the last equation and finally find Eqs. (35)–(39).

The flow equations (35)–(39) lead to the following fixed points:

$$2(z + D)\tilde{G}^{k,*}(t, t') = \mathcal{G}_k(t, t'),$$

$$2(2\alpha + D)\tilde{C}^{k,*}(t, t') = \mathcal{C}_k(t, t'),$$

$$2(2\alpha - D - 4z)D^{k,*}(t, t') = \mathcal{D}_k(t, t'),$$

$$4zR^{k,*}(t, t') = -\mathcal{R}_k(t, t'),$$

$$4z\Sigma^{k,*}(t, t') = -\mathcal{S}_k(t, t').$$

We replaced all  $Q_k$  quantities by these values in Eqs. (20) and (21), and found the final mode-coupling equations at the fixed point:

$$(z + D)\tilde{G}^{k,*}(t, t') = (D - z) \int_0^t dt_1 \tilde{G}_0^k(t, t_1) \left[ \int_0^{t_1} dt_2 R_k^*(t_1, t_2) \tilde{G}^{k,*}(t_1, t') + \int_0^{t_1} dt_2 \Sigma_k^*(t_1, t_2) \tilde{G}^{k,*}(t_2, t') \right],$$

$$(2\alpha + D)\tilde{C}^{k,*}(t, t') = (2\alpha + D - 2z) \int_0^t dt_1 \int_0^{t_1} dt_2 \tilde{G}^{k,*}(t, t_1) D_k^*(t_1, t_2) \tilde{G}^{k,*}(t', t_2).$$

These correspond to Eqs. (40) and (41) which are discussed in the main text.

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