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Langevin dynamics of the glass forming polymer melt: Fluctuations around the random phase approximation

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Abstract. In this paper the Martin-Siggia-Rose (MSR) functional integral representation is used for the study of the Langevin dynamics of a polymer melt in terms of collective variables: mass density and response field density. The resulting generating functional (GF) takes into account fluctuations around the random phase approximation (RPA) up to an arbitrary order. The set of equations for the correlation and response functions is derived. It is generally shown that for cases whenever the fluctuation-dissipation theorem (FDT) holds we arrive at equations similar to those derived by Mori-Zwanzig. The case when FDT in the glassy phase is violated is also qualitatively considered and it is shown that this results in a smearing out of the ideal glass transition. The memory kernel is specified for the ideal glass transition as a sum of all "water-melon" diagrams. For the Gaussian chain model the explicit expression for the memory kernel was obtained and discussed in a qualitative link to the mode-coupling equation.

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1 Introduction

Over the last decade the glass transition theory as well as corresponding experiments were strongly influenced by the mode coupling approach (MCA) [1,2]. This approach based on the Mori-Zwanzig projection formalism [3] specified for the two slow variables: mass density and longitudinal momentum density. The subsequent projection of the random forces, which are involved in the memory kernel, onto products of the two densities and the factorization of the resulting 4-point correlators yields the closed nonlinear equation for the density time correlation function $\phi(\mathbf{k}, t)$. The bifurcation analysis of this equation [1] shows that at some critical values of the coupling constants and control parameters (like temperature T, density n, *etc.*) the non-vanishing long time limit $\phi(\mathbf{k}, t \to \infty) = f(\mathbf{k})$ arises. This indicates the occurance of a non ergodic (glass) state.

A complementary approach based on the non-linear fluctuating hydrodynamic (NFH) was developed in [4–7]. The authors start here from a set of stochastic equations for the mass density and the momentum density. Then by using the renormalized perturbation theory and one-loop approximation they derive basically the same equations as in the MCA.

As distinct from the perturbative treatment the numerical solution of these equations is (with an accuracy of numerical errors) exact. Therefore, a comparison of the numerical solution with the perturbative results provides an estimation of the validity of the approximations made in the analytic studies. The results of these calculations [8,9] show that in spite of the fact that the time-dependent density correlation functions are slightly stretched the very important features, such as two-step relaxation regime, can not be obtained. This regime was reproduced in the numerical study of the Langevin equations of the system with a free-energy functional of the Ramakrishnan-Yussouf (RY) form [10]. The RY free energy functional provides a large number of glassy local minima, but from the results of reference [10] it is still not clear whether the observed two-step relaxation regime arises from non-linearities of density fluctuations in the liquid or from transitions between different glassy minima. Moreover, it is not evident how reliable the results of the NFH are near the main peak of the static structure factor $S(k)$, *i.e.* $k \approx k_0$. In this area the density fluctuations are rather strong and the correlator of the noise fields in reference [9,10] is taken artificially suppressed (the dimensionless parameter $\lambda = 10^{-4}$) otherwise the density could be even negative.

In this situation it is very instructive to start from the opposite, in some sense, to the NFH limit. In contrast to the NFH the random phase approximation (RPA) describes the modification of the behavior of free-particles by effective interactions. The dynamical version of the RPA

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was used mainly for the description of the dynamic spectrum of simple liquids [11] as well as for polymer melts and solutions [12–15]. As have been shown in reference [11] the basic defect of the RPA in the context of the glass transition problem is the absence of a central peak which is determined by the corresponding slow dynamic [1,2]. The reason of this is evident: the RPA completely ignores intermolecular collisions which only bring the system into a state of local thermodynamic equilibrium and eventually assure the hydrodynamic regime.

In the RPA the particles are free or only weakly interacting. Since these effects invariably dominate at sufficiently short wavelengths, such representation might be suitable for description at large wavelengths, $k \approx k_0$. To assure the feedback mechanism however, which is responsible for the glass transition [1,2] or the microphase separation in block copolymers [16–19], approaches beyond RPA are necessary.

For the static case it is such extension which was carried out in reference [18,19]. In reference [20] , by using a nonperturbative Hartree approximation, we have been able to derive a generalized Rouse equation for a tagged chain in a melt. The freezing process of the Rouse modes of the test chain was sequentially considered. In the present paper we emphasizes on a systematic way of taking into account density fluctuations in a homopolymer melt with respect to the dynamic RPA. In doing so the glass transition dynamics will be of our prime interest.This appears as a fundamental problem in polymer physics. The RPA is well known in describing several collective phenomena in interacting polymer systems quite well. The phase behavior (statics and dynamics) of polymer mixtures, block copolymer melts can be understood very well. The theoretical description of freezing processes, however, are certainly beyond the random phase approximations. Moreover, such freezing processes cannot be of perturbative nature. Interactions become strong and dominant on short length scales. Thus we must use methods that go systematically beyond the classical RPA in polymer physics. We must mention one important point here. So far we restrict ourselves to the cases of low molecular weight melts. This is to avoid additional complications with reptation dynamics for melts consisting of chains with a large degree of polymerization. Our point in this paper is thus to develop a method which allows to study the freezing of an ensemble of "Rouse chains" with a degree of polymerization below the critical molecular weight N_c.

The paper is organized as follows. In Section 2 the Langevin dynamics of a homopolymer melt is treated by using the Martin-Siggia-Rose (MSR) generating functional (GF) method [21,22]. The effective action is represented in terms of the two collective variables, the mass density and the response field density. In Section 3 the equations of motion for the time-dependent correlation function and the response function are derived. It is shown that in the regime when the fluctuation dissipation theorem (FDT) is valid these two equations are reduced to one, having the form of a MCA-equation, which yields under certain conditions an ideal glass transition. The case when the FDT is violated is also briefly considered. It is shown that by replacing the usual FDT by the assumption of a Quasi-FDT (QFDT) this leads to a smearing out of the ideal glass transition. In Section 4 the memory kernel for the Gaussian chain model is calculated explicitly and a closed equation for the non-ergodicity parameter is derived. Finally, Section 5 discusses the main results and perspectives.

2 The generating functional of a polymer melt in terms of the collective variables

Consider a homopolymer melt of M chains with the pth chain configuration at a time moment t characterized by the vector function $\mathbf{R}^{(p)}(s,t)$, where s numerates the segments of the chain, $0 \leq s \leq N$. The simultaneous dynamical evolution of $\mathbf{R}^{(p)}(s,t)$ is described by the Langevin equations

$$\xi_0 \frac{\partial}{\partial t} R_j^{(p)}(s,t) + \frac{\delta H\{R_j^{(p)}\}}{\delta R_j^{(p)}} = f_j^{(p)}(s,t) \qquad (1)$$

with the Hamiltonian

$$H\{\mathbf{R}\} = \frac{3T}{2l^2} \sum_{p=1}^{M} \int_0^N ds \left[\frac{\partial \mathbf{R}^{(p)}(s,t)}{\partial s}\right]^2 + \frac{1}{2} \sum_{p=1}^{M} \sum_{m=1}^{M} \int_0^N ds \times \int_0^N ds' V[\mathbf{R}^{(p)}(s,t) - \mathbf{R}^{(m)}(s',t)] \qquad (2)$$

and the random force correlator

$$\left\langle f_j^{(p)}(s,t) f_i^{(m)}(s',t')\right\rangle = 2T\xi_0 \delta_{pm} \delta_{ij} \delta(s-s') \delta(t-t') \qquad (3)$$

where ξ_0 denotes the bare friction coefficient and from now on the Boltzmann constant $k_b = 1$. The interaction function $V(r_1 - r_2)$ in equation (2) has the sense of a direct correlation function [11] for the monomers liquid.

After using the standard MSR-functional integral representation [21,22] for the system (1-3), the GF takes the form

$$\begin{aligned} Z\left\{l_j^{(p)}(s,t), \hat{l}_j^{(p)}(s,t)\right\} = & \\ \int \prod_{j=1}^{3} \prod_{p=1}^{M} & DR_j^{(p)}(s,t) D\hat{R}_j^{(p)}(s,t) \exp\left\{ A_0[R_j^{(p)}, \hat{R}_j^{(p)}] \right. \\ & + \frac{1}{2} \sum_{p=1}^{M} \sum_{m=1}^{M} \int dt \int_0^N ds\, ds' \int \frac{d^3k}{(2\pi)^3} i k_j i\hat{R}_j^{(p)}(s,t) V(k) \\ & \times \exp\left\{ i\mathbf{k}[\mathbf{R}^{(p)}(s,t) - \mathbf{R}^{(m)}(s',t)]\right\} + \sum_{p=1}^{M} \int dt \int_0^N ds \\ & \left. \times \left[R_j^{(p)}(s,t) l_j^{(p)}(s,t) - i\hat{R}_j^{(p)}(s,t) \hat{l}_j^{(p)}(s,t)\right] \right\} \end{aligned} \qquad (4)$$

where the MSR-action of the free chain system is given by

$$A_0\left\{R_j^{(p)},\hat{R}_j^{(p)}\right\} = \sum_{p=1}^{M}\int dt\int_0^N ds\Bigg\{T\xi_0[i\hat{\mathbf{R}}^{(p)}(s,t)]^2 + i\hat{R}_j^{(p)}(s,t)\left[\xi_0\frac{\partial}{\partial t}R_j^{(p)}(s,t) - \varepsilon\frac{\partial^2}{\partial s^2}R_j^{(p)}(s,t)\right]\Bigg\} \qquad (5)$$

where $\varepsilon = \dfrac{3T}{l^2}$ is the bare elastic modulus of a spring with the length of a Kuhn segment denoted by l, $V(k)$ is the Fourier transformation of $V(r_1 - r_2)$, $l_j^{(p)}$ and $\hat{l}_j^{(p)}$ are external fields conjugated to $R_j^{(p)}$ and $\hat{R}_j^{(p)}$ respectively and the summation over repeated Cartesian indices is implied. Now by the same way as in [23,24] collective variables can be introduced. As opposed to the statics [16–19] we need to consider not only the mass density

$$\rho(\mathbf{r},t) = \sum_{p=1}^{M}\int_0^N ds\,\delta(\mathbf{r} - \mathbf{R}^{(p)}(s,t)) \qquad (6)$$

but also the longitudinal projection of the response fields

$$\pi(\mathbf{r},t) = \sum_{p=1}^{M}\int_0^N ds\, i\hat{R}_j^{(p)}(s,t)\nabla_j\delta(\mathbf{r} - \mathbf{R}^{(p)}(s,t)) \qquad (7)$$

where again the summation over repeated Cartesian indices is implied. Then the GF (4) becomes

$$\begin{aligned}Z\{\cdots\} = &\int\prod_{p=1}^{M} D\mathbf{R}^{(p)}(s,t)D\hat{\mathbf{R}}^{(p)}(s,t)D\rho D\pi \\ &\times\delta\left[\rho(\mathbf{r},t) - \sum_{p=1}^{M}\int ds\,\delta(\mathbf{r} - \mathbf{R}^{(p)}(s,t))\right] \\ &\times\delta\left[\pi(\mathbf{r},t) - \sum_{p=1}^{M}\int ds\, i\hat{R}_j^{(p)}(s,t)\nabla_j\delta(\mathbf{r} - \mathbf{R}^{(p)}(s,t))\right] \\ &\times\exp\Bigg\{-\frac{1}{2}\int dt d^3r_1 d^3r_2\pi(\mathbf{r}_1,t)\rho(\mathbf{r}_2,t)V(\mathbf{r}_1 - \mathbf{r}_2) \\ &+A_0\left\{\mathbf{R}^{(p)},\hat{\mathbf{R}}^{(p)}\right\}\Bigg\}\end{aligned} \qquad (8)$$

where the dots imply some source fields which will be specified later.

It is convenient to introduce the 2-dimensional field

$$\rho_\alpha(1) = \begin{pmatrix}\rho(1)\\ \pi(1)\end{pmatrix} \qquad (9)$$

where $\alpha = 0, 1$ and $1 \equiv (\mathbf{r}_1, t_1)$ is used for abbreviation. In terms of the 2-dimensional density (9) the GF (8) takes an especially compact form

$$\begin{aligned}Z\{\psi_\alpha\} = &\int D\rho_\alpha(1) \\ &\times\exp\left\{-\frac{1}{4}\rho_\alpha(\bar{1})U_{\alpha\beta}(\bar{1}\bar{2})\rho_\beta(\bar{2}) + W\{\rho_\alpha\} + \rho_\alpha(\bar{1})\psi_\alpha(\bar{1})\right\}\end{aligned} \qquad (10)$$

with the action of the free system

$$\begin{aligned}W\{\rho,\pi\} = \ln&\int\prod_{p=1}^{M} D\mathbf{R}^{(p)}(s,t)D\hat{\mathbf{R}}^{(p)}(s,t) \\ &\times\exp\left\{A_0\{\mathbf{R}^{(p)},\hat{\mathbf{R}}^{(p)}\}\right\}\delta\left[\rho(\mathbf{r},t) - \sum_{p=1}^{M}\int ds\,\delta(\mathbf{r} - \mathbf{R}^{(p)}(s,t))\right] \\ &\times\delta\left[\pi(\mathbf{r},t) - \sum_{p=1}^{M}\int ds\, i\hat{R}_j^{(p)}(s,t)\nabla_j\delta(\mathbf{r} - \mathbf{R}^{(p)}(s,t))\right]\end{aligned} \qquad (11)$$

and the 2×2-interaction matrix

$$U_{\alpha\beta}(1,2) = \begin{pmatrix}0 & V(|\mathbf{r}_1 - \mathbf{r}_2|)\\ V(|\mathbf{r}_1 - \mathbf{r}_2|) & 0\end{pmatrix} \qquad (12)$$

and the $\psi_\alpha(1)$ is a source field conjugated to the 2-density (9). In equation (10) and below the summation over repeated Greek indices and integration over variables with bars is implied.

The exact form of the action $W\{\rho_\alpha\}$ is not known explicitly, but can be obtained by a functional expansion by assuming that the density fluctuations are not very large and the functional $W\{\rho_\alpha\}$ is convex.

The calculation is quite similar to the static case [16–18]. Let us introduce the cumulant GF, the "free energy", of the free system

$$\begin{aligned}F\{\psi_\alpha\} &\equiv \ln Z_0\{\psi_\alpha\} \\ &= \ln\int D\rho_\alpha\ \exp\left\{W\{\rho_\alpha\} + \rho_\alpha(\bar{1})\psi_\alpha(\bar{1})\right\}.\end{aligned} \qquad (13)$$

This GF has the expansion

$$\begin{aligned}F\{\psi_\alpha\} = &F_\alpha^{(1)}(\bar{1})\psi_\alpha(\bar{1}) + \frac{1}{2!}F_{\alpha\beta}^{(2)}(\bar{1}\bar{2})\psi_\alpha(\bar{1})\psi_\beta(\bar{2}) \\ &+\frac{1}{3!}F_{\alpha\beta\gamma}^{(3)}(\bar{1}\bar{2}\bar{3})\psi_\alpha(\bar{1})\psi_\beta(\bar{2})\psi_\gamma(\bar{3}) + \ldots\end{aligned} \qquad (14)$$

with the *free system* cumulant correlators

$$F_\alpha^{(1)}(1) = \frac{\delta}{\delta\psi_\alpha(1)}F\{\psi_\alpha\}\Bigg|_{\psi=0} \qquad (15)$$

$$F_{\alpha\beta}^{(2)}(1,2) = \frac{\delta^2}{\delta\psi_\alpha(1)\delta\psi_\beta(2)}F\{\psi_\alpha\}\Bigg|_{\psi=0} \qquad (16)$$

$$F_{\alpha\beta\gamma}^{(3)}(1,2,3) = \frac{\delta^3}{\delta\psi_\alpha(1)\delta\psi_\beta(2)\delta\psi_\gamma(3)}F\{\psi_\alpha\}\Bigg|_{\psi=0}. \qquad (17)$$

We are searching for the action $W\{\rho_\alpha\}$ in the form of an expansion

$$\begin{aligned}W\{\rho_\alpha\} = &W\{\langle\rho_\alpha\rangle_0\} + \frac{1}{2!}W_{\alpha\beta}^{(2)}(\bar{1}\bar{2})\delta\rho_\alpha(\bar{1})\delta\rho_\beta(\bar{2}) \\ &+\frac{1}{3!}W_{\alpha\beta\gamma}^{(3)}(\bar{1}\bar{2}\bar{3})\delta\rho_\alpha(\bar{1})\delta\rho_\beta(\bar{2})\delta\rho_\gamma(\bar{3}) + \ldots\end{aligned} \qquad (18)$$

where

$$\delta\rho_\alpha(1) = \rho_\alpha(1) - \langle\rho_\alpha(1)\rangle_0 = \rho_\alpha(1) - F_\alpha^{(1)}(1). \tag{19}$$

In order to determine the coefficients in the expansion (18) one should use the saddle point method when calculating the functional integral (13). This can be carried out in the same spirit as in references [17,18]. This results in a Legendre transformation with respect to the extremum field $\bar{\rho}_\alpha(1)$:

$$F\{\psi_\alpha\} = W\{\bar{\rho}_\alpha\} + \bar{\rho}_\alpha(\bar{1})\psi_\alpha(\bar{1}). \tag{20}$$

As a result [25] it is found:

$$\bar{\rho}_\alpha(1) = \frac{\delta F\{\psi_\alpha\}}{\delta\psi_\alpha(1)} \tag{21}$$

$$\psi_\alpha(1) = -\frac{\delta W\{\bar{\rho}_\alpha\}}{\delta\bar{\rho}_\alpha(1)}\cdot \tag{22}$$

By the use of the expansions (14) and (18) in equations (21, 22) we can relate the coefficients $W^{(n)}$ with the free system cumulant correlators [16,25]

$$W_{\alpha\beta}^{(2)}(1,2) = -\left[\left(F^{(2)}\right)^{-1}\right]_{\alpha\beta}(1,2) \tag{23}$$

$$W_{\alpha\beta\gamma}^{(3)}(1,2,3) = F_{\alpha\beta\gamma}^{(3)\,amp.}(1,2,3) \tag{24}$$

$$\begin{aligned} W_{\alpha\beta\gamma\delta}^{(4)}(1,2,3,4) = F_{\alpha\beta\gamma\delta}^{(4)\,amp.}(1,2,3,4) - F_{\alpha\beta\bar{\gamma}}^{(3)\,amp.}(1,2,\bar{3}) \\ \times F_{\bar{\gamma}\bar{\bar{\gamma}}}^{(2)}(\bar{3}\bar{\bar{3}})F_{\bar{\bar{\gamma}}\gamma\delta}^{(3)\,amp.}(\bar{\bar{3}},3,4) \end{aligned} \tag{25}$$

where the so called amputated correlators are defined by the relation [25]:

$$\begin{aligned} &F_{\alpha\beta\cdots\delta}^{(n)\,amp.}(1,2,\ldots,n) = \\ &\quad\left(F^{(2)}\right)_{\alpha\bar{\alpha}}^{-1}(1,\bar{1})\cdots\left(F^{(2)}\right)_{\delta\bar{\delta}}^{-1}(n,\bar{n})F_{\bar{\alpha}\cdots\bar{\delta}}^{(n)\,amp.}(\bar{1}\ldots,\bar{n}). \end{aligned} \tag{26}$$

The main result of this section is the GF (10) given now by

$$\begin{aligned} Z\{\psi_\alpha\} = \\ &\int D\delta\rho_\alpha \exp\Bigg\{-\frac{1}{2}\left[U+F^{(2)\,-1}\right]_{\alpha\beta}(\bar{1},\bar{2})\delta\rho_\alpha(\bar{1})\delta\rho_\beta(\bar{2}) \\ &+\frac{1}{3!}W_{\alpha\beta\gamma}^{(3)}(\bar{1}\bar{2}\bar{3})\delta\rho_\alpha(\bar{1})\delta\rho_\beta(\bar{2})\delta\rho_\gamma(\bar{3}) \\ &+\frac{1}{4!}W_{\alpha\beta\gamma\delta}^{(4)}(\bar{1}\bar{2}\bar{3}\bar{4})\delta\rho_\alpha(\bar{1})\delta\rho_\beta(\bar{2})\delta\rho_\gamma(\bar{3})\delta\rho_\delta(\bar{4}) + \ldots \\ &+\rho_\alpha(\bar{1})\psi_\alpha(\bar{1})\Bigg\} \end{aligned} \tag{27}$$

where the coefficients in the effective action are expressed in terms of free polymer system dynamics and given by equations (23-25, 26). The relation (27) is the dynamical generalization of the coarse grained partition function which was obtained (for a diblock copolymer melt) in the references [17,18].

3 The equations of motion for the time correlation and response function

The representation of the GF (27) is a good starting point for taking into account fluctuation effects which enable us to go beyond the standard RPA methods. Before we proceed in this direction let us rederive the simple RPA-results for convenience and as a consistency check.

3.1 RPA results

If we restrict ourselves in the expansion (27) to the quadratic order, then the RPA-correlator and response function $S_{\alpha\beta}(1,2)$ is obtained as a 2×2-matrix form

$$S_{\alpha\beta}(1,2) = \left[\hat{U} + \hat{F}^{(2)\,-1}\right]_{\alpha\beta}^{-1}(1,2). \tag{28}$$

Here $\hat{U}$ is the matrix of interactions and given by equation (12). The correlation 2×2-matrix of the free system has the form

$$F_{\alpha\beta}^{(2)}(1,2) = \begin{pmatrix} F_{00}^{(2)}(1,2) & F_{10}^{(2)}(1,2) \\ F_{01}^{(2)}(1,2) & 0 \end{pmatrix}\cdot \tag{29}$$

In equation (29) off diagonal elements $F_{01}^{(2)}(1,2)$, $F_{10}^{(2)}(1,2)$ are retarded and advanced susceptibilities respectively; the diagonal element $F_{00}^{(2)}(1,2)$ is the density correlator. The relation between them is determined by the FDT in $(\mathbf{k},t)$-representation

$$\beta\frac{\partial}{\partial t}F_{00}^{(2)}(\mathbf{k},t) = F_{01}^{(2)}(\mathbf{k},t) - F_{10}^{(2)}(\mathbf{k},t) \tag{30}$$

or alternatively in $(\mathbf{k},\omega)$-representation

$$\beta i\omega F_{00}^{(2)}(\mathbf{k},\omega) = F_{10}^{(2)}(\mathbf{k},\omega) - F_{01}^{(2)}(\mathbf{k},\omega) \tag{31}$$

where $\beta = 1/T$. The inversion of the 2×2-matrix in equation (28) results in the matrix elements in the $(\mathbf{k},\omega)$-representation

$$S_{00}(\mathbf{k},\omega) = \frac{F_{00}^{(2)}(\mathbf{k},\omega)}{\left[1+V(k)F_{10}^{(2)}(\mathbf{k},\omega)\right]\left[1+V(k)F_{01}^{(2)}(\mathbf{k},\omega)\right]} \tag{32}$$

$$S_{01}(\mathbf{k},\omega) = \frac{F_{01}^{(2)}(\mathbf{k},\omega)}{1+V(k)F_{01}^{(2)}(\mathbf{k},\omega)} \tag{33}$$

$$S_{10}(\mathbf{k},\omega) = \frac{F_{10}^{(2)}(\mathbf{k},\omega)}{1+V(k)F_{10}^{(2)}(\mathbf{k},\omega)}\cdot \tag{34}$$

From equations (32-34) we can simply see that the FDT for the non-interacting system (30, 31) assures the validity of FDT in RPA

$$\beta i\omega S_{00}(\mathbf{k},\omega) = S_{10}(\mathbf{k},\omega) - S_{01}(\mathbf{k},\omega). \tag{35}$$

Equations (32-34) coincide with the classical expressions for RPA-susceptibilities which have been used in the theory of liquids (see *e.g.* Eqs. (2.7.42) in [11]) and more frequently in the dynamic theory of polymer melts [13–15].

3.2 Equations of motion beyond RPA: Role of fluctuations

In this general case the full renormalized correlator $2 \times 2-$matrix $G_{\alpha\beta}(1,2)$ must satisfy the Dyson equation [29]

$$\left[G^{-1}\right]_{\alpha\beta}(1,2) = \left[S^{-1}\right]_{\alpha\beta}(1,2) - \Sigma_{\alpha\beta}(1,2) \tag{36}$$

where the so called self-energy functional $\Sigma_{\alpha\beta}(1,2)$ contains only one-line irreducible diagrams (or diagrams which cannot be disconnected by cutting only one line) [25]. These diagrams are built up from the vertices given by the effective action (27) and lines with the full correlator matrix $G_{\alpha\beta}(1,2)$ assigned to them. The diagrams which are relevant for the glass transition problem will be discussed later.

The self-energy matrix has the triangular block structure

$$\Sigma_{\alpha\beta}(1,2) = \begin{pmatrix} 0 & \Sigma_{10}(1,2) \\ \Sigma_{01}(1,2) & \Sigma_{11}(1,2) \end{pmatrix} \cdot \tag{37}$$

Inversion of the Dyson equation (36) yields the result

$$G_{00}(\mathbf{k},\omega) = \frac{S_{00}(\mathbf{k},\omega)S_{01}^{-1}(\mathbf{k},\omega)S_{10}^{-1}(\mathbf{k},\omega) + \Sigma_{11}(\mathbf{k},\omega)}{\left[S_{01}^{-1}(\mathbf{k},\omega) - \Sigma_{10}(\mathbf{k},\omega)\right]\left[S_{10}^{-1}(\mathbf{k},\omega) - \Sigma_{01}(\mathbf{k},\omega)\right]} \tag{38}$$

$$G_{01}(\mathbf{k},\omega) = \frac{1}{S_{01}^{-1}(\mathbf{k},\omega) - \Sigma_{10}(\mathbf{k},\omega)} \tag{39}$$

$$G_{10}(\mathbf{k},\omega) = \frac{1}{S_{10}^{-1}(\mathbf{k},\omega) - \Sigma_{01}(\mathbf{k},\omega)} \cdot \tag{40}$$

If besides relation (35) FDT is also valid for the full correlator and response functions

$$\beta i\omega G_{00}(\mathbf{k},\omega) = G_{10}(\mathbf{k},\omega) - G_{01}(\mathbf{k},\omega) \tag{41}$$

or in time domain

$$\beta \frac{\partial}{\partial t} G_{00}(\mathbf{k},t) = G_{01}(\mathbf{k},t) - G_{10}(\mathbf{k},t) \tag{42}$$

then the exact self-energy obeys

$$\beta i\omega \Sigma_{11}(\mathbf{k},\omega) = \Sigma_{01}(\mathbf{k},\omega) - \Sigma_{10}(\mathbf{k},\omega) \tag{43}$$

or correspondingly in the time domain

$$\beta \frac{\partial}{\partial t} \Sigma_{11}(\mathbf{k},t) = \Sigma_{10}(\mathbf{k},t) - \Sigma_{01}(\mathbf{k},t). \tag{44}$$

This agrees with the corresponding relations for self-energy given in [26]. We stress that the FDT for the free system (31) as well as in RPA (35) is always valid. For the full correlator and response functions of a glass forming system this is not obligatory the case [27–29].

In order to proceed further let us use for the free system correlator the diffusional approximation [30]

$$F_{00}^{(2)}(\mathbf{k},t) = F_{st}(\mathbf{k})e^{-k^2 D(\mathbf{k})t} \tag{45}$$

where $D(\mathbf{k}) = D_0/g(\mathbf{k})$, $D_0 = T/\xi_0$, $g(\mathbf{k})$ is a polymer static structure fuctor and $F_{st}(\mathbf{k})$ is the corresponding static correlator. Then taking into account FDT (31) we have

$$F_{00}^{(2)}(\mathbf{k},\omega) = \frac{2k^2 D(\mathbf{k})F_{st}(\mathbf{k})}{\omega^2 + (k^2 D(\mathbf{k}))^2} \tag{46}$$

$$F_{01}^{(2)}(\mathbf{k},\omega) = -\frac{\beta k^2 D(\mathbf{k})F_{st}(\mathbf{k})}{-i\omega + k^2 D(\mathbf{k})} \tag{47}$$

$$F_{10}^{(2)}(\mathbf{k},\omega) = -\frac{\beta k^2 D(\mathbf{k})F_{st}(\mathbf{k})}{i\omega + k^2 D(\mathbf{k})} \cdot \tag{48}$$

One should use equations (46-48) in the RPA-result (32-34), then the expressions for the full correlator and response functions (38-40), after going back to the time domain, yields

$$\left[\tau_c \frac{\partial}{\partial t} + \chi_{st}^{-1}(\mathbf{k})\right] G_{01}(\mathbf{k};t,t') + \int_{t'}^{t} \Sigma_{10}(\mathbf{k};t,t'')G_{01}(\mathbf{k};t'',t')dt'' = -\delta(t-t') \tag{49}$$

$$\left[\tau_c \frac{\partial}{\partial t} + \chi_{st}^{-1}(\mathbf{k})\right] G_{00}(\mathbf{k};t,t') + \int_{-\infty}^{t} \Sigma_{10}(\mathbf{k};t,t'')G_{00}(\mathbf{k};t'',t')dt'' + \int_{-\infty}^{t} \Sigma_{11}(\mathbf{k};t,t'')G_{10}(\mathbf{k};t'',t')dt'' = -2T\tau_c G_{10}(\mathbf{k};t,t'). \tag{50}$$

In the equations (49-50) the inverse RPA-static susceptibility

$$\chi_{st}^{-1}(\mathbf{k}) = \left[\beta F_{st}(\mathbf{k})\right]^{-1} - V(k) \tag{51}$$

and the bare correlation time

$$\tau_c = \frac{1}{\beta k^2 D F_{st}(\mathbf{k})} = \frac{\xi_0}{k^2 \rho_0} \tag{52}$$

where ρ_0 is the average segments concentration. The initial conditions for the equations (49, 50) has the form

$$\begin{aligned} \tau_c G_{01}(\mathbf{k};t=t'+0^+) &= -1 \\ G_{01}(\mathbf{k};t=t') &= 0 \end{aligned} \tag{53}$$

and

$$G_{00}(\mathbf{k};t=t') = G_{st}(\mathbf{k}) \tag{54}$$

where $G_{st}(\mathbf{k})$ is the full static correlator. Equations (49,50) represent the general result of the present paper, and below we will discuss the physical aspects of them in more detail at specific examples.

The resulting equations (49-54) are indeed very general. We made only use of the diffusional approximation for the free system correlator (45) and of a causality condition. Qualitatively the same equations of motion was obtained in the dynamical Hartree approximation for a test chain in a melt (see Eqs. (29-32) in [20]) and for a manifold in a random medium (see Eqs. (7-9) in [31] and Eqs. (B3-B5) in [32]). Let us now consider the case when besides equations (49-54) the FDT (42) for the full correlator and response function holds.

3.3 Time-homogeneity and FDT for the full matrix $\mathbf{G}_{\alpha\beta}(\mathbf{k};\mathbf{t})$ hold

Let us assume in equation (50) $t' = 0$ and $t > 0$. Then after differentiation of both sides of equation (50) with respect to the time and taking into account FDT (42) we have

$$\left[\tau_c \frac{\partial}{\partial t} + \chi_{st}^{-1}(\mathbf{k})\right] G_{01}(\mathbf{k};t) + \int_0^t \Sigma_{10}(\mathbf{k};t-t') G_{01}(\mathbf{k};t')dt' + \int_{-\infty}^{\infty} dt' \left\{\beta \frac{\partial}{\partial t}\Sigma_{11}(\mathbf{k};t-t') - \Sigma_{10}(\mathbf{k};t-t')\right\} G_{10}(\mathbf{k};t') = 0. \tag{55}$$

The comparison of the equation (55) with the equation (49) yields

$$\beta \frac{\partial}{\partial t}\Sigma_{11}(\mathbf{k};t) = \Sigma_{10}(\mathbf{k};t) \tag{56}$$

which is again the familiar relation (44) for $t > 0$. As it should be the case, one of the equations (49, 50) is getting redundant now.

Using the equations (42, 44) in equation (50) and after integration by part we arrive at the result

$$\left[\tau_c \frac{\partial}{\partial t} + \tilde{\chi}_{st}^{-1}(\mathbf{k})\right] G_{00}(\mathbf{k};t) + \beta \int_0^t \Sigma_{11}(\mathbf{k};t-t') \frac{\partial}{\partial t'} G_{00}(\mathbf{k};t')dt' = 0 \tag{57}$$

where

$$\tilde{\chi}_{st}^{-1}(\mathbf{k}) = \left[\beta F_{st}^{(2)}(\mathbf{k})\right]^{-1} - V(\mathbf{k}) - \beta\Sigma_{11}(\mathbf{k};t=0). \tag{58}$$

The last term in equation (58) is the contribution of fluctuations in the static correlation function. It must be stressed that equation (57) is equivalent to the Mori-Zwanzig equation, derived by the projection formalism [3] and was specified for the two slow variables, mass density and longitudinal momentum density, in reference [1]. Performing the Laplace-transformation

$$\mathcal{L}(\cdots) = \int_0^{\infty} dt \ldots \exp(izt) \tag{59}$$

in equation (57) for $\phi(\mathbf{k},z) \equiv G_{00}(\mathbf{k},z)/G_{st}(\mathbf{k})$ we get

$$\phi(\mathbf{k},z) = \frac{1}{-iz + \dfrac{k^2 G_{st}^{-1}(\mathbf{k})}{\tau_0 + k^2 M(\mathbf{k},z)}} \tag{60}$$

where

$$\tau_0 = \frac{\xi_0}{T\rho_0} \tag{61}$$

$$M(\mathbf{k},z) = \beta^2 \Sigma_{11}(\mathbf{k},z) \tag{62}$$

and we have used the relation

$$\tilde{\chi}_{st}^{-1} = T G_{st}^{-1}(\mathbf{k}). \tag{63}$$

The interesting point is that the self-energy matrix element Σ_{11} is proportional to the memory-kernel. Indeed equation (62) connects the Mori-Zwanzig technique with the MSR-formalism. The particular form of the self-energy matrix element Σ_{11} for the physical problem defined by the action given by equation (27) will be discussed in the Section 4.

It can be expected that a critical temperature T_c exists where the correlator $G_{00}(\mathbf{k},z)$ as well as the memory kernel acquire a pole at $z = 0$. This would show an ergodicity breaking or an ideal glass transition [1] and will be considered in Section 4.

3.4 The time-homogeneity is valid but FDT is violated

This case was discussed in the literature [27,32,33]. The more general case, when the time-homogeneity does not hold any more was also considered [28,29].

According the scenario given in [27,32,33] below the temperature T_c of the ergodicity breaking the phase space decomposes into regions (ergodic components). The latter are separated by high barriers which can not be crossed at times $t < t^*$. The time t^* has the physical meaning of a "trapping" time. Especially for a system with infinite range interactions, we have $t^* \to \infty$ in the thermodynamic limit. This point had become most obvious in the case of spin glasses with long range interactions [27]. In such systems quenched disorder is present from the beginning and it has been shown that replica symmetry breaking corresponds to the splitting of the phase space by infinite high barriers. The present dynamical theory on conventional glasses without quenched disorder suggests a similar scenario. Disorder develops during cooling and eventually large barriers develop. Then these barriers cannot be crossed and the phase space is broken up into accessible parts. Dynamics becomes slow and glassy. Mathematically this is monitored in the invalidity of the FDT.

To be more precise, we assume that for our case t^* is large but still finite. For the intervals $t \ll t^*$ the relaxation occurs within one ergodic component, the dynamics is ergodic and FDT holds. For $t \gg t^*$ the system jumps over the phase space barriers from one component to another and FDT is violated. In this case the total response to an external field consists of two parts. One of them is determined by the dynamics inside one ergodic component (intracomponent dynamics) obeying FDT, and the other which appears at $t > t^*$ as a result of crossing the barriers between different components (inter-component dynamics). The latter process violates the usual FDT.

With this in mind let us make the following assumption

$$\beta\left[\frac{\partial}{\partial t}+\gamma \mathrm{sign}(t)\theta(|t|-|t^*|)\right]G_{00}(\mathbf{k},t)=G_{01}(\mathbf{k},t)-G_{10}(\mathbf{k},t) \tag{64}$$

which might be the linear version of a more general relation

$$\beta\left[\frac{\partial}{\partial t}+\gamma X\{G_{00}(\mathbf{k},t)\}\right]G_{00}(\mathbf{k},t)=G_{01}(\mathbf{k},t)-G_{10}(\mathbf{k},t). \tag{65}$$

In equations (64, 65) the (phenomenological) parameter γ has the dimension of an inverse time and, as we will see below, has the meaning of a characteristic rate of the inter-component dynamics ("hopping process" in the nomenclature of Ref. [2]). $X\{G_{00}\}$ is an arbitrary functional of the correlator $G_{00}(\mathbf{k},t)$. In equation (64) $\theta(\cdots)$ is the θ-function and sign(t) keeps the correct transformation under time reversal: $G_{01}(-t) = G_{10}(t)$. We will call equations (64, 65) after references [32,33] Quasi-FDT (QFDT).

Let us use equation (64) (at $t > t^* > 0$) in equation (50) (at $t' = 0$ and $t > 0$) by acting with $\beta(\partial/\partial t+\gamma)$ on its both sides. After the same calculations carried out already in Section 3.3 we arrive at

$$\beta\left(\frac{\partial}{\partial t}+\gamma\right)\Sigma_{11}(\mathbf{k};t) = \Sigma_{10}(\mathbf{k};t) \tag{66}$$

where $t > t^* > 0$. As before, the equation (66) assures that one of the equations (49, 50) gets redundant, whenever the QFDT (64) is valid.

The substitution of equations (64, 66) into equation (50) yields

$$\begin{aligned}\left[\tau_c\frac{\partial}{\partial t}+\tilde{\chi}_{st}^{-1}\right]&G_{00}(\mathbf{k};t)\\ &+\beta\int_0^t \Sigma_{11}(\mathbf{k};t-t')\frac{\partial}{\partial t'}G_{00}(\mathbf{k};t')dt'\\ &+2\beta\gamma\int_{-\infty}^{-t^*} \Sigma_{11}(\mathbf{k};t-t')G_{00}(\mathbf{k};t')dt'\\ &+\beta\gamma\int_{-t^*}^{t-t^*} \Sigma_{11}(\mathbf{k};t-t')G_{00}(\mathbf{k};t')dt' = 0.\end{aligned} \tag{67}$$

Two important limiting cases can be distinguished:

- If $t \to \infty$ and $t^* \to \infty$, but $t/t^* \to 0$, then the two last terms in equation (67) can be neglected and we go back to equation (50), which contains (under conditions discussed in Sect. 4) an ideal glass transition. The system could never escape from one ergodic component (an absolutely confined component in nomenclature of Ref. [34]).
- If $t \to \infty$ and t^* is large but finite, (so that $t^*/t \to 0$), then the next to last term in the l.h.s. of equation (67) can be neglected. In this case the equation (67) takes the form

$$\begin{aligned}\left[\tau_c\frac{\partial}{\partial t}+\tilde{\chi}_{st}^{-1}\right]&G_{00}(\mathbf{k};t)\\ &+\beta\int_0^t \Sigma_{11}(\mathbf{k};t-t')\left(\frac{\partial}{\partial t'}+\gamma\right)G_{00}(\mathbf{k};t')dt' = 0.\end{aligned} \tag{68}$$

The Laplace transformation of equation (68) gives the result

$$\phi(\mathbf{k},z) = \frac{1}{-iz+\gamma+\dfrac{k^2\bar{\chi}_{st}^{-1}(k)/T}{\tau_0+k^2M(\mathbf{k},z)}} \tag{69}$$

with

$$\bar{\chi}_{st}^{-1} = \tilde{\chi}_{st}^{-1} - \gamma\tau_c. \tag{70}$$

In contrast to the ideal glass transition case at $z \to 0$ the kernel $M(\mathbf{k},z)$ is large but finite. Then , according equation (69) at $z \to 0$ the behavior of $\phi(\mathbf{k},z)$ is determined mainly by a simple pole at $iz = \gamma$. Instead of going to a plateau the correlator $\phi(\mathbf{k},t)$ decays with the characteristic rate γ. This is a result of the inter-component dynamics.

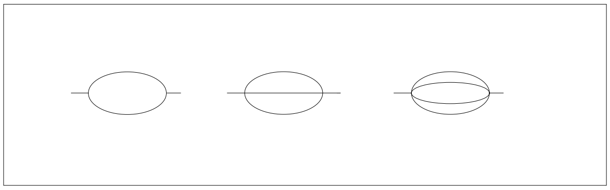

Fig. 1. Diagrammatic representation of the self-energy $\Sigma_{11}(\mathbf{k},z)$ in MCA, which has a simple pole at $z = 0$, *i.e.* is relevant for the ideal glass transition. The vertices are bare: $W^{(3)}, W^{(4)}$, ..., *i.e.* this approximation neglects all vertex renormalization.

4 The explicit form for the memory Kernel M(k, z). The mode-coupling approximation

For the ideal glass transition problem [1,2] the correlator $G_{00}(\mathbf{k},z)$ as well as the memory kernel $M(\mathbf{k},z)$ acquire a pole at $z = 0$ at the critical temperature T_c. One can easily see that for the effective action, given by equation (27), such contribution come from the sum of all "water-melon" diagrams which are represented in Figure 1. Each line denotes the full matrix $G_{\alpha\beta}(\mathbf{k},z)$ and a vertex with m legs denotes the bare vertex function $W^{(m)}_{\alpha\beta\ldots\gamma}(\mathbf{k}_1,z_1;\mathbf{k}_2,z_2;\ldots\mathbf{k}_m,z_m)$. In the MCA all vertices renormalization is neglected [35].

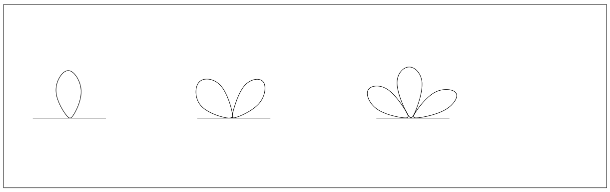

Fig. 2. The sum of all tadpole diagrams, which are finite at the external frequency $z \to 0$. They are not relevant for the glass transition problem.

Another type of diagram, the "tadpole" diagrams, which are shown in Figure 2, appears in the context of a Hartree-approximation [32,33,36]. On the other hand the contributions of these diagrams remain finite at $z \to 0$ and because of this they are not relevant for the ideal glass transition problem. On the contrary, these diagrams are essential in the context of *e.g.* fluctuation effects in the theory of microphase separation in block copolymers [18, 19]. It was shown there, that fluctuations change the order of the phase transition from two (mean field) to one (upon renormalization). In this research field the corresponding procedure has been terminated as Brazovskii renormalization.

The explicit expression for the arbitrary vertex function $W^{(n)}_{\alpha\beta\dots\gamma}(1,2,\dots,n)$ is not known in detail and one can not sum up all "water-melon" diagrams. That is why in the spirit of MCA we restrict ourselves only to the first diagram given in Figure 1, which corresponds to the one-loop approximation. As a result we have

$$\Sigma_{11}(\mathbf{k};z) = 2(\frac{1}{3!})^2 \int \frac{d^4q}{(2\pi)^4} W^{(3)}_{1\bar{\alpha}\bar{\beta}}(k,k-q,q) \times G_{\bar{\alpha}\bar{\gamma}}(k,k-q) G_{\bar{\beta}\bar{\delta}}(q) W^{(3)}_{\bar{\gamma}\bar{\delta}1}(q,k-q,k) \quad (71)$$

where the short hand notation, $k \equiv (\mathbf{k}, z)$ and $q \equiv (\mathbf{q}, s)$, was used and the expression for the vertex function has the specific form

$$W^{(3)}_{\alpha\beta\gamma}(1,2,3) = F^{(3)}_{\bar{\alpha}\bar{\beta}\bar{\gamma}}(\bar{1},\bar{2},\bar{3}) F^{(2)-1}_{\bar{\alpha}\alpha}(\bar{1},1) F^{(2)-1}_{\bar{\beta}\beta}(\bar{2},2) F^{(2)-1}_{\bar{\gamma}\gamma}(\bar{3},3). \quad (72)$$

In general there are nine terms in the sum (71), but only one of them, which does not include a response function has the important $1/z$-singularity at $z \to 0$. This leads to the expression

$$\Sigma_{11}(\mathbf{k},z) = 2(\frac{1}{3!})^2 \int \frac{d^4q}{(2\pi)^4} W^{(3)}_{100}(k,k-q,q) G_{00}(k-q) \times G_{00}(q) W^{(3)}_{001}(q,k-q,k) \quad (73)$$

where

$$W^{(3)}_{100}(k,k-q,q) = F^{(3)}_{011}(k,k-q,q)(F^{(2)-1})_{01}(k) \times (F^{(2)-1})_{10}(k-q)(F^{(2)-1})_{10}(q) \quad (74)$$

and

$$W^{(3)}_{001}(q,k-q,k) = F^{(3)}_{110}(q,k-q,k)(F^{(2)-1})_{10}(q) \times (F^{(2)-1})_{10}(k-q)(F^{(2)-1})_{01}(k). \quad (75)$$

In equation (73) the integrals over Laplace-frequency s is taken along the straight line in the complex s-plane above all singularities of the integrand. Since a pole of $G_{00}(\mathbf{q}, s)$ at $s = 0$ predetermines the $1/z$-behavior of the whole integral, we are able to consider the vertex functions $W^{(3)}_{100}$ and $W^{(3)}_{001}$ only in the static limit, $s \to 0$ and $z \to 0$. Below, we give these limits for the 2- and 3-point response functions.

The Laplace transformation of the 3-point response function, which appears in equation (74), is given by equation (A.6) in the Appendix. As a result its static limit reads as

$$\lim_{z_2,z_3 \to 0} F^{(3)}_{011}(\mathbf{k}_2, z_2; \mathbf{k}_3, z_3) = \beta^2 F^{(3)}_{st}(\mathbf{k_2}, \mathbf{k_3}). \quad (76)$$

The static limit of the 3-point response function, which appears in equation (75) has the same form

$$\lim_{z_2,z_3 \to 0} F^{(3)}_{110}(z_1, z_2) = \beta^2 F^{(3)}_{st}(\mathbf{k_1}, \mathbf{k_2}). \quad (77)$$

The static limit for the 2-point response functions is given by the relation

$$\lim_{z \to 0} F^{(2)}_{01}(\mathbf{k}, z) = \lim_{z \to 0} F^{(2)}_{10}(\mathbf{k}, z) = -\beta F_{st}(\mathbf{k}). \quad (78)$$

Explicitly the expressions for $F^{(3)}_{st}$ and $F^{(2)}_{st}$ are given by [38]:

$$F^{(3)}_{st}(\mathbf{K}_1, \mathbf{K}_2) = -\frac{1}{2} N^2 \rho_0 \left\{ \frac{J_2(\mathbf{K}_1^2) - J_2(\mathbf{K}_2^2)}{\mathbf{K}_1^2 - \mathbf{K}_2^2} + \frac{J_2(\mathbf{K}_2^2) - J_2(\mathbf{K}_3^2)}{\mathbf{K}_2^2 - \mathbf{K}_3^2} + \frac{J_2(\mathbf{K}_3^2) - J_2(\mathbf{K}_1^2)}{\mathbf{K}_3^2 - \mathbf{K}_1^2} \right\} \quad (79)$$

with

$$\mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3 = 0 \quad (80)$$

and

$$F^{(2)}_{st}(\mathbf{K}) = N \rho_0 J_2(\mathbf{K}^2) \quad (81)$$

where $\mathbf{K} = \mathbf{k} l \sqrt{N/6}$ and $\rho_0 = cN$ is the average segments concentration. The function

$$J_2(x) = 2 \frac{e^{-x} - 1 + x}{x^2} \quad (82)$$

is known as the Debye function in polymer physics and is usually approximated well by the more simple Padé expression [30,38]

$$J_2(x) \approx \frac{1}{1 + \frac{1}{2}x} \cdot \quad (83)$$

By making use of equations (79-83) the expression for the vertices (74,75) in the static limit becomes

$$W_{st}^{(3)}(\mathbf{K}_1,\mathbf{K}_2,\mathbf{K}_3) = -\frac{1}{4\beta\rho_0^2 N}\left[3+\frac{1}{2}(\mathbf{K}_1^2+\mathbf{K}_2^2+\mathbf{K}_3^2)\right] \tag{84}$$

where $\mathbf{K}_i^2 = \mathbf{k}_i^2 l^2 N/6$. Then for the memory kernel (62) we derive

$$\begin{aligned} M(\mathbf{k},z) = & 2\left(\frac{1}{4!}\right)^2 \frac{1}{\rho_0^4 N^2}\int\frac{d^3q\,ds}{(2\pi)^4}\left[3+\frac{Nl^2}{6}(k^2+q^2+\mathbf{kq})\right]^2 \\ & \times G_{st}(-\mathbf{k}-\mathbf{q})G_{st}(\mathbf{q})\phi(-\mathbf{k}-\mathbf{q},-z-s)\phi(\mathbf{q},s). \end{aligned} \tag{85}$$

The integral over q is mainly determined by the strong peak of $G_{st}(\mathbf{q})$ at $q = q_0 = 1/\sigma$, where σ is the bead diameter in the spring-bead model for the chains in the melt. In that case the second term in the brackets dominates and N-dependence for long chains is cancelled, as it should be.

In the glass state the correlator $\phi(\mathbf{k},z)$ has the form

$$\lim_{z\to 0}\phi(\mathbf{k},z) = \frac{f(\mathbf{k})}{-iz} \tag{86}$$

where $f(\mathbf{k})$ is the non-ergodicity parameter. From equations (60, 85) one can easily see that the function $f(\mathbf{k})$ satisfies the equation

$$\begin{aligned} \frac{f(\mathbf{k})}{1-f(\mathbf{k})} = & 2\left(\frac{1}{4!6}\right)^2\left(\frac{l}{\rho_0}\right)^4 G_{st}(\mathbf{k}) \\ & \times\int\frac{d^3q}{(2\pi)^4}[k^2+q^2+\mathbf{kq}]^2 G_{st}(-\mathbf{k}-\mathbf{q})G_{st}(\mathbf{q})f(-\mathbf{k}-\mathbf{q})f(\mathbf{q}) \end{aligned} \tag{87}$$

which qualitatively corresponds to the result of the conventional MCT although the kernel of the integral part has a different form (see *e.g.* Eq. (3.37) in Ref. [1]). In reference [1] on the basis of bifurcation theory the solution of integral equations of this type has been analyzed in full details. It was in particular shown that a positive solution for the non-ergodicity parameter exists provided that the kernel of the integral part is positive and symmetric in k and q (see Sects. 3.6 and 3.7 in [1]). One can see that equation (87) fits these conditions. It has been also shown in [1] that close to the bifurcation point all correlations obey the universal scaling behavior. We are not in a position to discuss here the different scenarios of the idealized glass transition and better religate readers to reference [1].

The factor l^4 in front of the mode-coupling integral (87) indicates that the relevant length scale for the glass area is indeed the Kuhn segment length. This confirms statements, that in polymer melts, where a large variety and wide range of internal degrees of freedom dominate the physical behavior the glass transition is indeed ruled on local scales, *i.e.*, the range of the nearest neighbor interactions. Moreover, the present model suggests, that the glass area is larger for stiffer chains, since l becomes larger. This is qualitatively correct but needs a more detailed investigation.

5 Summary and discussion

In this paper we have shown that the MSR-functional integral representation is very convenient for the treatment of the Langevin dynamics of the polymer melt in terms of the collective variables: the mass density and the response field density. The expansion of the free energy and the Legendre transformation technique, which was given in the references [16–18] for the static case, was extended here for the dynamics. As a result we have derived the dynamical GF (27) with the action that allow results beyond the RPA up to arbitrary order of the density and/or response fields density.

It was shown that the GF is a good starting point for the derivation of the general dynamical equations. This is the set of equations (49, 50) for the correlation and response functions, with the free part determined by RPA. For the particular case when the time-homogeneity and FDT are satisfied these two equations reduce to the one equation (57).

It is obvious that equation (57) is equivalent to the Mori-Zwanzig equation with the memory kernel given by the matrix element $\Sigma_{11}(\mathbf{k},t)$. In the framework of the Mori-Zwanzig formalism and MCA the glass transition problem was extensively discussed in [1,2]. In our approach these results are qualitatively restored if the "water-melon" diagrams for $\Sigma_{11}(\mathbf{k},z)$ (see Fig. 1) are summarized. The results of the vertices renormalization could be in principle also investigated [39].

The situation when FDT is violated is much more obscure in spite of the extensive discussion [27–29,32,33]. It could be guessed that the physical reason for this (at least at a finite t^*) is an intercomponent dynamics as it was discussed in Section 4.4. We have made a simple but plausible assumption about the form of QFDT (64). When this assumption was made in the corresponding model calculation we had shown that a sharp (or ideal) glass transition is smeared out by this intercomponent dynamics with a characteristic rate γ and the density correlator takes the form (69).

For the ideal glass transition case we have calculated the expression for the memory kernel (85) by using the explicit forms for the free system's static correlators. As a result the equation (87) for the non-ergodicity parameter $f(\mathbf{k})$ is qualitatively the same like in MCA. The physical picture we had derived here is most interesting. We have indeed shown that the violation of the fluctuation dissipation theorem yields a similar picture as in systems where quenched disorder is present from the beginning. For example in spin glasses it was shown, that the presence of disorder and frustration yields a glassy phase. Moreover it could be shown that the case of replica symmetry breaking is responsible for the disordered nature of the phase space, especially for the large barriers dividing the phase space. Thus the entire phases space is no longer accessible for the system. This corresponds *e.g.* to glassy dynamics. In structural glasses such as polymer melts which form easily glasses, quenched disorder is not present. In the melt phase equilibrium dynamics determines the structural properties, even though the dynamics is very slow mainly ruled by the molecular weight. Here we must start from equations that take into account all interactions. With the formalism presented in the sections above we succeeded to derive a similar picture on totally different physical grounds. We had shown that glassy phases could appear upon violation of the FDT. At a simple model computation we had presented arguments, that a characteristic time t^* can be related to barrier heights that eventually can be crossed. This corresponds to the breaking of the phase space into different regions that are separated by barriers, which have their origin in the interactions. In fact, these barriers correspond to the development of a multi valley structure of the phase space. We will come back to this point in later publications.

The present general formalism allows important generalizations for interacting systems. For example we will treat homopolymer blends and copolymer melts which tremendously enriches the picture of the dynamical behavior. The dynamics of copolymers was studied above a microphase separation temperature T_{ms} in RPA [14,15] and below T_{ms} by the numerical solution of the Ginzburg-Landau equation [40]. One can easily derive a copolymer counterpart of the dynamical GF (27). Then the Hartree approximation, or summation of all tadpole diagrams shown in Figure 2 (in the same manner as for the static [18, 19]) gives a direct way to obtain a closed dynamical equation for the composition-composition correlation function. Moreover we have now the possibility to study the glass transition in blends and copolymer melts. These problems are of wide experimental interest. Imagine for example that one component of the blend or one species of the copolymer melt freezes out during cooling. The striking problem is then to discuss the interplay between freezing and phase – or microphase – separation. The dynamics of one species becomes very slow and some parts of the systems become eventually immobile at certain correlation length, corresponding to the distance of the (ideal) critical point. These problems are also under current investigation.

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Appendix: The 3-point response function and its Laplace transformation

The 3-point response function which appears in equation (74) is determined by

$$
\begin{aligned}
&F^{(3)}_{011}(\mathbf{k}_1,t_1;\mathbf{k}_2,t_2;\mathbf{k}_3,t_3) = \\
&\quad (ik_2)_j(ik_3)_l \sum_{p_1,p_2,p_3=1}^{M} \int_0^N ds_1 ds_2 ds_3 \\
&\quad \times \Big\langle i\hat{R}_j^{(p_2)}(s_2,t_2) i\hat{R}_l^{(p_3)}(s_3,t_3) \exp\Big\{ i\mathbf{k}_1\mathbf{R}^{(p_1)}(s_1,t_1) \\
&\quad + i\ \mathbf{k}_2\mathbf{R}^{(p_2)}(s_2,t_2) + i\mathbf{k}_3\mathbf{R}^{(p_3)}(s_3,t_3)\Big\}\Big\rangle_0 \qquad \text{(A.1)}
\end{aligned}
$$

where $\langle\cdots\rangle_0$ stands for the averaging with the action of the free chain system. By making use of the Nonlinear-FDT (NFDT) rule (see Eq. (2.31) in Ref. [37])

$$
-i\hat{R}_j(s,t) \longrightarrow \beta \frac{\partial}{\partial t} R_j(s,t) \qquad \text{(A.2)}
$$

we will come to the following relation

$$
\begin{aligned}
&F^{(3)}_{011}(\mathbf{k}_1,t_1;\mathbf{k}_2,t_2;\mathbf{k}_3,t_3) = \\
&\qquad \beta^2 \frac{\partial^2}{\partial t_2 \partial t_3} F^{(3)}_{000}(\mathbf{k}_1,t_1;\mathbf{k}_2,t_2;\mathbf{k}_3,t_3) \qquad \text{(A.3)}
\end{aligned}
$$

with the causality condition $t_1 > \{t_2, t_3\}$. In the same way we get

$$
\begin{aligned}
&F^{(3)}_{110}(\mathbf{k}_1,t_1;\mathbf{k}_2,t_2;\mathbf{k}_3,t_3) = \\
&\qquad \beta^2 \frac{\partial^2}{\partial t_1 \partial t_2} F^{(3)}_{000}(\mathbf{k}_1,t_1;\mathbf{k}_2,t_2;\mathbf{k}_3,t_3) \qquad \text{(A.4)}
\end{aligned}
$$

with the causality condition $t_3 > \{t_1, t_2\}$.

Let us define the Laplace-transformation of the 3-point response function

$$
\begin{aligned}
F^{(3)}_{011}(z_1,z_2,z_3) &= \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_1} dt_3 F^{(3)}_{011}(t_1,t_2,t_3) \\
&\quad \times \exp\{iz_1t_1 + iz_2t_2 + iz_3t_3\} \\
&= 2\pi\delta(z_1+z_2+z_3) \int_{-\infty}^{0} dt_{21} \\
&\quad \times \int_{-\infty}^{0} dt_{31} F^{(3)}_{011}(t_{21},t_{31}) \exp\{iz_2t_{21} + iz_3t_{31}\} \\
&= 2\pi\delta(z_1+z_2+z_3) F^{(3)}_{011}(z_2,z_3) \qquad \text{(A.5)}
\end{aligned}
$$

where we have used the causality condition $t_1 > \{t_2, t_3\}$ and the time translational invariance.

By making use of the NFDT (A.4) and after integrations by parts we have

$$
\begin{aligned}
F^{(3)}_{011}(\mathbf{k}_2,z_2;\mathbf{k}_3,z_3) = \beta^2 \Big\{ & F^{(3)}_{st}(\mathbf{k}_2,\mathbf{k}_3) \\
& - iz_2 F^{(3)}_{000}(\mathbf{k}_2,z_2;\mathbf{k}_3,t_{31}=0) \\
& - iz_3 F^{(3)}_{000}(\mathbf{k}_2,t_{21}=0;\mathbf{k}_3,z_3) \\
& + (iz_2)(iz_3) F^{(3)}_{000}(\mathbf{k}_2,z_2;\mathbf{k}_3,z_3) \Big\}
\end{aligned}
\qquad \text{(A.6)}
$$

where

$$
\begin{aligned}
&F^{(3)}_{000}(\mathbf{k}_2,z_2;\mathbf{k}_3,z_3) = \\
&\int_{-\infty}^{0} dt_{31} \int_{-\infty}^{0} dt_{21} F^{(3)}_{000}(\mathbf{k}_2,t_{21};\mathbf{k}_3,t_{31}) \exp\{iz_2t_{21} + iz_3t_{31}\}
\end{aligned}
\qquad \text{(A.7)}
$$

and

$$F^{(3)}_{000}(\mathbf{k}_2, z_2; \mathbf{k}_3, t_{31} = 0) = \int_{-\infty}^{0} dt_{21} F^{(3)}_{000}(\mathbf{k}_2, t_{21}; \mathbf{k}_3, t_{31} = 0) \exp\{iz_2 t_{21}\} \quad \text{(A.8)}$$

and $F^{(3)}_{st}(\mathbf{k}_2, \mathbf{k}_3)$ is the static 3-point density correlator. From equation (A.6) we immediately obtain the static limit (76).

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