

Polymers: When $S(Q,t)$ is not what you think ! The role of dynamic RPA

Michael Monkenbusch^{1,*}

¹Jülich Centre for Neutron Science (JCNS), Forschungszentrum Jülich GmbH, Jülich, Germany

Abstract. Investigating a (polymeric) soft-matter system with several components often is aimed at the observation of the motions/mobilities of one of the components. The normal approach to this request in the context of quasielastic neutron scattering (e.g. NSE) is to put contrast on the targeted component, typically by leaving it hydrogenated and have the rest (surrounding, matrix) deuterated. In simple systems with only one molecular species as a homo-polymer melt with a few of the molecules contrasted (e.g. 10% h in 90% d) -provided the h- and d-molecular varieties behave sufficiently equal- this strategy yields a valid single chain (molecule) structure factor $S(Q,t)/S(Q)$, even for a 50/50% mixture. However, if the component of interest and the matrix are of different kind, unexpected distortions of the observed $S(Q,t)$ may occur. Interpretation of such results in terms of the single chain structure factor would then lead to erroneous conclusions. In this contribution the conditions, under which these distortions will occur, are discussed and how dynamic RPA may help to cope with them is explained. A practical method to apply this correction to polymer and similar problems is presented and an experimental verification is discussed [1, 12].

1 Introduction

Neutron scattering investigations of polymers often rely on the use of mixtures of different molecule types. Most common is the mixture of deuterated and protonated species of otherwise identical polymers in order to create contrast in the small-angle scattering (SANS) regime. Further sophistication may comprise the combination of different molecular architectures (e.g. stars, branched, dendrimers ...) or partially labeled chain or -the simplest- different lengths (e.g. molecular weights). While for the interpretation of SANS results it is common practice to use random-phase-approximation (RPA) derived expression to describe the scattering data [2–4], it usually is ignored if the dynamics is inferred from intermediate scattering functions $S(Q, t)$ as obtained by neutron spin-echo spectroscopy (NSE). In SANS investigations the mutual interaction differences as expressed by a Flory-Huggins parameter χ enter the RPA expression for the intensity as in Eq. 1

$$I(Q) = \Delta\rho^2 \frac{1}{[\phi S_1(Q)]^{-1} + [(1 - \phi)S_2(Q)]^{-1} - 2\chi} \quad (1)$$

with the structure functions $S_{1,2}(Q)$ of the two components, ϕ the volume fraction of component 1 and $\Delta\rho$ the scattering length density contrast between components 1 and 2. Depending on the value of χ enhanced critical scattering as precursor of demixing may be observed and may be used to infer χ . But also (independent on χ) different architectures of components 1 and 2 lead to the final form of $I(Q)$ and thus have to be accounted for during the extraction of model parameters, which is realized by Eq. 1 with $\chi = 0$. A simple case for linear flexible polymers

*e-mail: m.monkenbusch@fz-juelich.de

with different lengths but $\chi = 0$ is illustrated in figure 1, where some intermediate intensity at low Q is observed

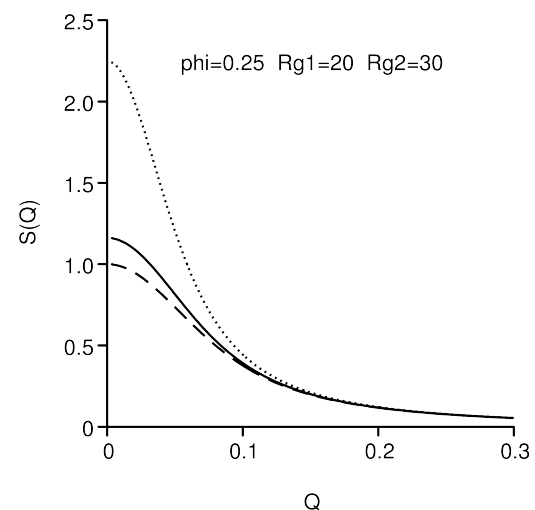


Figure 1. Comparison of the "static" scattering functions of short and long flexible linear polymers (Gaussian coils) and a mixture of both (solid line) as computed using the RPA expression Eq. 1 and $\phi = 0.25$.

in the resulting scattering due to combination of contributions from both components, at larger Q the behaviour of $S_i(Q)$ for both components are the same and coincide. This is true for the whole Q -range if the only difference of components 1 and 2 is the scattering contrast (d-, or h-labeled). In that case the RPA solely gives rise to the standard concentration pre factor $\phi(1 - \phi)$. This situation also

was and is given in a larger number of NSE investigations with a mixture of just differently labelled but otherwise equal molecular species. Usually the preparations are also such that $\chi \approx 0$ may be assumed. In that case there is no further need to observe RPA effects in the observed dynamic intermediate scattering functions. However, let us now contemplate the situation of a chain mixture as depicted in figure 2 more closely. Representative a labelled (minority and short) chain in yellow-green and a longer (majority-matrix) chain in blue are shown. From the point of view of the "labelled" green chain the contrast background is dominated by the blue matrix chains, however, diluted by a finite (small) probability that in any surrounding volume element another green chain can be found (indicated by the little green triangular fillings). Without further specific interactions, i.e. $\chi = 0$ these are randomly occupied and just give rise to the $(1 - \phi)$ term in the intensity pre factor. On the other hand from the point of any one long blue chains the same matrix scattering "dilution" also is present and yields a contrast and thus visibility to the long chains. These effects are described by Eq. 1. At larger Q , where typically most NSE experiments probe the scattering this obviously has little to no influence on the shape of $I(Q)$.

But now let us consider the resulting time dependence of $I(Q, t)$. If both components relax in the same way the resulting time function will be the same and no extra effects would have to be taken into account. However, if the relaxation is significantly different there will be contributions from the labelled (short) chains and from the somewhat visible long "matrix"-chains, then with different time functions. The extreme cases can easily be guessed: if the matrix chain are completely immobile and static there will be no relaxation of the short chains visible since even with mobile short chains the contrast modulation pattern will not change. On the other hand for extremely mobile matrix chains we expect to just "see" the dynamics of the short chains. In between some sort of combination is to be expected. It would be tempting to just enter $S_i(Q, t)$ instead of $S_i(Q)$ into Eq. 1, but as is shown below this is not the right approach.

While in the last decades some approaches on the use of dynamical RPA have been made [5–10] these did not directly yield a way to routinely describe the full resulting intermediate scattering curves as e.g. obtained in NSE experiments and allow model fitting within this framework. In this contribution an approach is described that establishes this.

2 Result for non-interacting 3-component system

To cover most cases of NSE experiments RPA expressions for an $n = 2$ system with an extra matrix component was considered and implemented [1]. For a system of $n + 1$ (interacting) components, a matrix (polymer) and n (different) polymers with different contrasts with respect to the matrix/solvent yields a $n \times n$ matrix problem: In the static formulation this implies:

$$\mathbf{S}(Q)^{-1} = \mathbf{S}^0(Q)^{-1} + \mathbf{v}(Q) \quad (2)$$

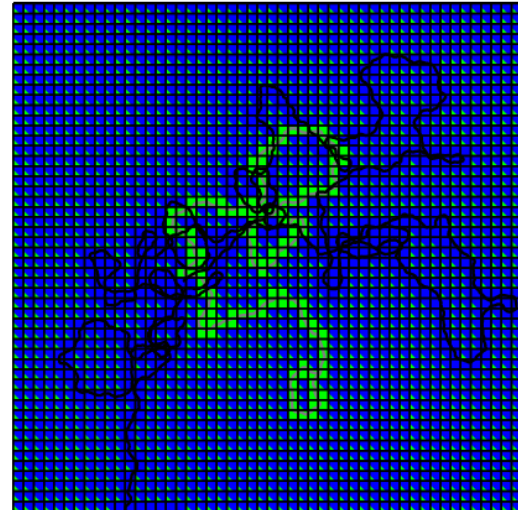


Figure 2. Sketch of the contrast situation -highlighted by the traces of one chain of each species" in a mixture of chains with different scattering length density (indicated by colors green and blue). Occupancy of "blue" and "green" segments of "other" chains simply governed by their volume fractions is indicated by the fraction green triangles in these cells- of chain occupancy (simple RPA) at cells occupied by other chains. Yielding large "matrix" contrast for the minority ($\phi = 0.2$) short, "green" chains and lesser but nonzero contrast for the majority, "blue" chains. The mutually created visibility leads to crosstalk of the relaxation dynamics of bot chains in the scattering signal, which may be described using dynamic RPA.

$\mathbf{S}^0(Q)$ is the matrix of the individual scattering functions and $\mathbf{v}(Q)$ includes the interaction between the components (here incompressibility i.e. mutual exclusion repulsion only). Then the scattering intensity $I(Q)$ from a system with contrast $\mathbf{a} = \{\rho_1 - \rho_c, \rho_2 - \rho_c\}$ between the components and the matrix is

$$I(Q) = \mathbf{a}^T \mathbf{S}(Q) \mathbf{a} \quad (3)$$

This is the standard expression used for SANS evaluation. Already decades ago Akcasu and Tombakoglu [11] extended the RPA treatment to include dynamics yielding the Laplace transform of the dynamic scattering matrix $\mathbf{S}(Q, s)$:

$$\mathbf{S}(Q, s) = [\mathbf{1}s + Q^2 \mathbf{D}(Q, s)]^{-1} \mathbf{S}(Q) \quad (4)$$

in terms of a frequency dependent diffusion coefficient:

$$\mathbf{D}^0(Q, s) = \frac{1}{Q^2} ([\mathbf{S}^0(Q, s) \mathbf{S}^0(Q)^{-1}]^{-1} - \mathbf{1}) \quad (5)$$

with the relation between the undisturbed free diffusion coefficient $\mathbf{D}^0(Q, s)$ and the RPA influenced $\mathbf{D}(Q, s)$:

$$\mathbf{D}(Q, s) \approx [\mathbf{1} + Q^2 \mathbf{D}^0(Q, s) \mathbf{S}^0(Q) \mathbf{v}'(Q, s)]^{-1} \times \mathbf{D}^0(Q, s) [\mathbf{1} + \mathbf{S}^0(Q) \mathbf{v}(Q)] \quad (6)$$

with the incompressibility related interaction term

$$\mathbf{v}' = (\beta/s) [\chi_{cc}^0(Q, s)^{-1} - \chi_{cc}^0(Q, s = 0)^{-1}] \mathbf{J} \mathbf{E} \mathbf{E}^T \quad (7)$$

($\beta = 1/k_B T$ cancels out from the final expression), and $\mathbf{E}\mathbf{E}^T$ is a matrix with all elements equal to 1, the index cc relates to the "invisible" matrix, most a deuterated "background" compound. The dynamic susceptibility $\chi(Q, s)$ corresponds to the time derivative of $S(Q, t)$ the scattering functions $\chi(Q, s) = -\beta dS(Q, t)/dt = -\beta [sS(Q, s) - S(Q, t = 0^+)]$. With $\mathbf{v}(Q) = (\beta/\chi_{cc}^0)\mathbf{E}\mathbf{E}^T + \epsilon$ this yields the dynamic RPA result over the full time range using the undisturbed dynamic structure functions $S_{ii}^0(Q, t)$ of the components and the matrix function $S_{cc}^0(Q, t)$ as inputs, where the index c stands for the matrix (background) component. Focussing on the interference effects resulting from incompressibility any small potential interaction parameters $\epsilon_{i,j}$ are ignored. This largely holds for labelled mixtures of h- and d-labelled molecules assembled from the same types of monomers.

Reducing the general treatment to a 3 = (2+1) component system with volume fractions $\phi_1 + \phi_2 + \phi_3 = 1$ ($c=3$). We use:

$$\hat{S}_i = \phi_i S_{ii}^0(Q) \quad (8)$$

and the Laplace transforms

$$S_{ii}^0(Q, s) = S_{ii}^0(Q) F_i(Q, s) \quad (9)$$

as expressed by the Q -dependent, normalized function $f_i = F_i(Q, s)$.

For the polymer type relaxations it is possible to approximate $f(s)$ using:

$$f(s) = \left(\sum_{i=1}^N A_i \right)^{-1} \sum_{i=1}^N \frac{A_i}{r_i + s} \quad (10)$$

the coefficients A_i and rates r_i have to be derived from fitting the full model functions $S(Q, t)$ to the corresponding sum of exponentials for each Q .

The matrix elements S_{11} of the Laplace transformed scattering matrix \mathbf{S} then is:

$$S_{11} = S_1 \times \frac{[f_1 \tilde{f}_2 S_2^2 + f_2 \tilde{f}_1 S_2 S_1 + f_c \tilde{f}_1 S_c S_1 + f_1 (\tilde{f}_2 + \tilde{f}_c) S_c S_2 + S_c^2 \tilde{f}_c f_1]}{(S_1 + S_2 + S_c) [\tilde{f}_2 S_2 + \tilde{f}_1 S_1 + \tilde{f}_c S_c]} \quad (11)$$

with

$$\tilde{f}_i(s) = f_i(s) s - 1 = \mathcal{L}\{d(S_i^0(Q, t)/S_i^0(Q))/dt\} \quad (12)$$

For the 1-component labelled $\Delta\rho^2 S_{11}(Q, t)$ represents the observed echo amplitude in an NSE experiment. More complicated labellings require the full \hat{S} matrix, but to discuss the salient features we may resort to just S_{11} . And next the analytically solvable combination of two components with simple exponential relaxations with different rates (time constants) is illuminated in order to highlight some basic properties of the dynamic RPA.

3 Simple exponential combination

For time functions $f_i(t) = \exp(-t r_i)$ resulting in $f_i(s) = 1/(s + r_i)$ the inverse Laplace transform of Eq. 11 can be performed analytically yielding Eq. 13.

Note that this is different from plainly inserting $S(\dots, t)$ into the SANS RPA expression Eq. 1, which would yield Eq. 15! The proper dynamic RPA result for this generic simple case

$$S(\dots, t) = \frac{S_1 S_2 \phi (1 - \phi)}{\phi S_1 + (1 - \phi) S_2} e^{-t r_{\text{RPA}}} \quad (13)$$

is just another single exponential relaxation decay, however, with a modified relaxation rate r_{RPA} :

$$r_{\text{RPA}} = \frac{r_1 r_2 [S_1 \phi + S_2 (1 - \phi)]}{r_1 S_1 \phi + r_2 S_2 (1 - \phi)} \quad (14)$$

which is in contrast to the outcome of the **wrong(!)** direct combination of $S_i(Q, t)$ using the SANS expression:

$$S^{\text{static RPA}}(\dots, t) = \frac{S_1 S_2 \phi (1 - \phi)}{\phi S_1 e^{t r_2} + (1 - \phi) S_2 e^{t r_1}} \quad (15)$$

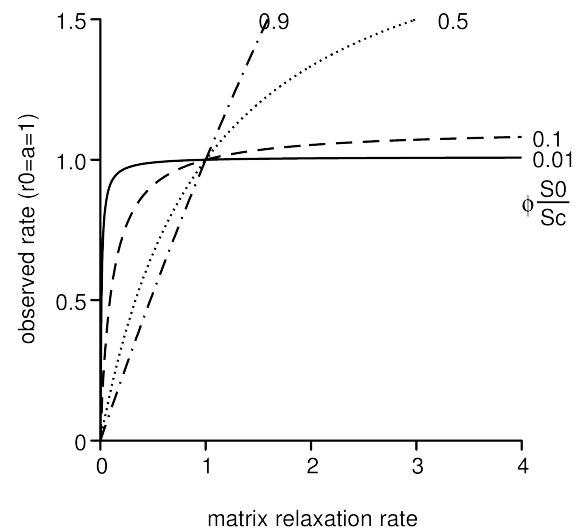


Figure 3. Resulting exponential decay rate for a hypothetical mixture of chains with different simple exponential relaxations. The example shows the dependence of the observed rate r_{RPA} as function of a matrix relaxation rate $r_{\text{matrix}} = r_c = r_2$ for fixed $r_0 = r_1 = 1$ different curves pertain to different ratios $\phi S_0(Q)/[(1 - \phi) S_c(Q)]$

Figure 3 illustrates the dependence of the resulting observed relaxation rate r_{RPA} as function of the rate of the second component (here=matrix) for different scattering contributions of the components $\phi S(Q)$ (labelled) and $(1 - \phi) S_c(Q)$ (matrix); for the figure the relaxation rate of the first component is set to 1. The salient feature can directly be extracted: (i) an immovable embedding ($r_c = 0$) in any case also yields a relaxation free resulting scattering, no dynamics is observable, all shown curves meet at (0,0). (ii) in the limit $\phi \rightarrow 0$ the observed relaxation rate soon approaches the undisturbed relaxation rate of the labelled component (here $r_1 = 1$). (iii) vice versa for $\phi \rightarrow 1$ the rate approaches that of the then dominant matrix. (iv)

the crossing of all curves at (1,1) indicates that no change in relaxation (i.e. no distortion of experimental conclusions) is to be expected if the dynamics of both components are equal (very similar).

Note: all changes of the relaxation functions discussed here and throughout this paper only pertain effects that relate to the visibility of molecular movements imposed by the contrast setting in combination with the incompressibility constraint.

This does **not include** any mutual influence on the molecular mobilities as expressed in $S_i^0(Q, t)$. These are subject to modelling or other analysis after the here discussed "distortions" due to their coupling to the observable scattering intensity has been accounted for. The latter is the role of the here discussed dynamic RPA influence!

3.1 Numerics aspects

While the evaluation of Eq. 11 is straightforward the subsequent requirement of an inverse Laplace transform to arrive at $I(Q, t)$ is not. If the single component scattering functions $S(Q, s)$ are just known numerically or as real functions the inversion is impractical. However, if $S(Q, s)$ could be obtained on a complex path as used in the Mellin Laplace inversion

$$\mathcal{L}^{-1}\{f(s)\} = \frac{1}{i2\pi} \int_{\xi-i\infty}^{\xi+i\infty} f(s)e^{st} ds \quad (16)$$

the inversion becomes numerically feasible. The required analytic property can be achieved by an intermediate evaluation step that maps the model functions $S_i(Q, t)$ to a sum of simple exponentials, the resulting Laplace transform Eq. 10 than can be inserted into Eq. 11 to yield the required analytic continuation of $S(Q, s)$. The determination of the exp-sum for any given relaxation function, e.g. computed from a suitable polymer scattering model, is automatically done in the software module developed for the dynamic RPA fitting procedure described in ref [1] and used in the following examples. Figure 4 illustrates the N-dependence of achievable accuracy of the N-exp-sum representation of test functions that resemble typical relaxation curves as observed for polymer dynamics over a time span of 6 decades.

Note that limitation in the numeric procedure require the restriction to a minimum value of the individual rates (in order to stay away from nearly divergent $1/(s+a)$ contributions). However, selecting this limit (if it applies) to more than an order of magnitude beyond the longest observed time keeps the associated error of the results low.

4 An experimental verification

The development of a practical implementation of the described dynamics RPA correction was triggered by the observation of "strange" behaviour in the results of an experiment intended to investigate the dynamics of short tracer polymer chains in a matrix of long reptating polyethylene (PE) chains [12] and in analog way for polyethyleneoxide (PEO) [13]. The data exhibit a leveling off of the relaxation curves at long times which are incompatible with the behaviour of diffusing small molecules with the macroscopic diffusion also established by PFG-NMR.

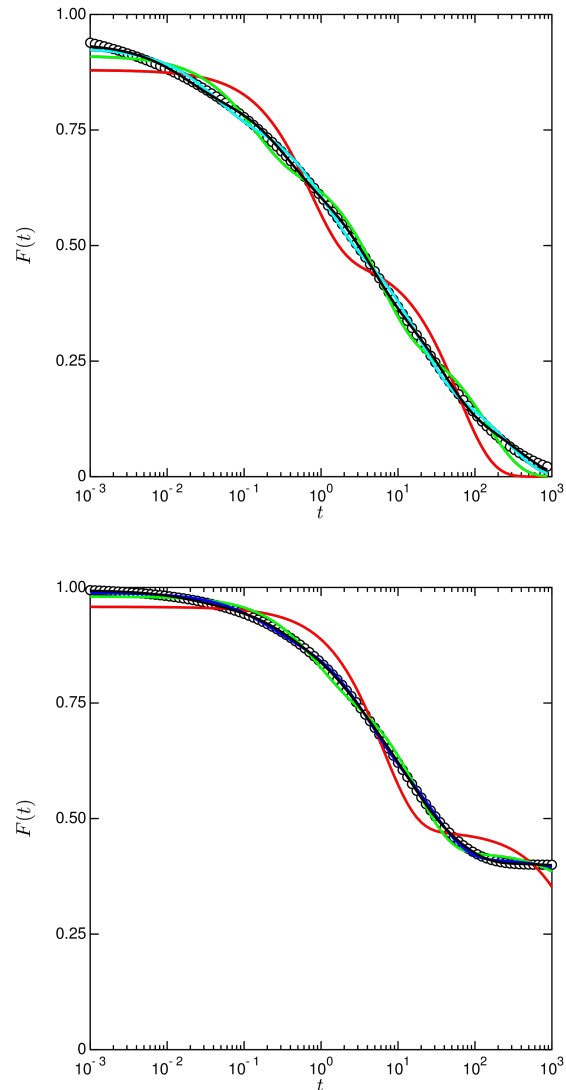


Figure 4. Example sequence of n-exp fits for increasing accuracy requirements (colored lines) as obtained by the automatism used in the software implementation of the dynamic RPA procedure [1]. The text functions (symbols) were: $\exp(-0.3t)$ and $0.6 \exp(-0.5t) + 0.4$. The black lines represent the final result obtained with 5 resp. 6 simple exponentials.

As it turns out the observation is not related to "bad" experiments with excessive background scattering and unsuitable background subtraction or may need other strange explanations but can quantitatively be described within the above described dynamic RPA algorithm. Figure 5 shows a representative example of these data for a concentration $\phi = 0.12$ of the h-labeled tracer polymers in the d-labeled long chain matrix. This concentration yields a clearly visible contribution of the slower long chains in terms of a retardation at longer times more or less halting at a plateau like level. This is in contrast to the expectation for the "pure" diffusion dominated relaxation of the tracers (red lines) which swiftly approaches zero at long observation times.

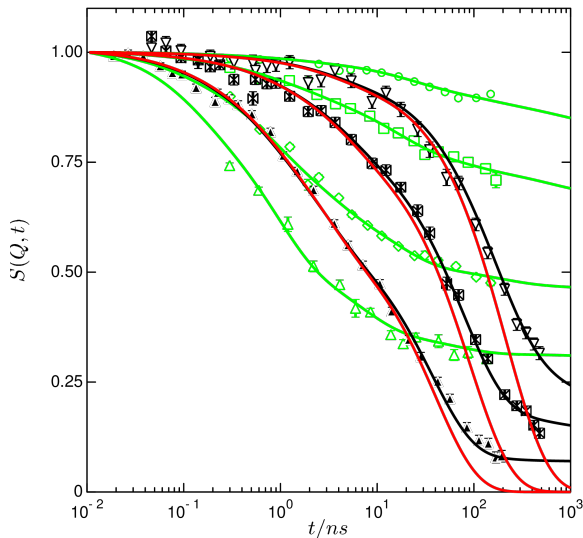


Figure 5. Fits of the scattering function of labelled small PE-tracer molecules (black) consisting of an initial sub-linear diffusion and Rouse dynamics with non-Gaussian effects [12] after including the dynamic RPA influence of the long chain matrix (green symbols and lines). The tracer volume fraction was $\phi = 0.12$, the long chain influence leads to excess residual amplitudes at large Q as the comparison with the computation without RPA-effects ($\phi \rightarrow 0$, red lines) clearly shows. The Q -values for the tracers are: 0.05, 0.078 and 0.12 \AA^{-1} and for the long chains: 0.05, 0.077, 0.115 and 0.145 \AA^{-1} .

The details of the sub-linear tracer diffusion thus could be extracted from the data by fitting the model function (a product of a diffusion expression and a Rouse mode sum) to the data by observing the dynamic RPA effects that depend on the knowledge of the structure function of the long chains. The details of this treatment are given in ref. [12].

Note that by augmenting the experiment with runs on inversely labelled samples containing a fraction of h-labelled long chains in an otherwise d-labelled systems (e.g. 10% h-long, 78% d-long and 12% d-short) would allow also assessing potential influences of the short chain dilution on the long chains and thus enhance the accuracy of the whole procedure. In the present case the 12% volume fraction is on the limit where such effects would start to significantly influence the results. Again it has to be emphasized that the dynamic RPA treatment only pertains the visibility effects due to the interference of the intermingled incompressible polymers. Any alteration of the chain dynamics due to hindering, topological interaction or added friction by the presence of the "other" polymers still must be modelled into the "undisturbed" $S_i^0(Q, t)$ structure functions; these are determined (by model refinement) by fitting within the dynamic RPA framework as explained here.

5 Some hypothetical extrapolations

As already mentioned in the introduction a completely immobile matrix would not allow any visible scattering length density variations with time and thus no relaxation in the scattering functions even if the tracer are very mobile. To test this case the fit results of figure 5 have been taken and recomputed but now with a slowing factor of 10^6 for the long chain matrix functions. As figure 6 illustrates this pushes all observed scattering functions close to the static line $S(Q, t)/S(Q, t = 0) = 1$.

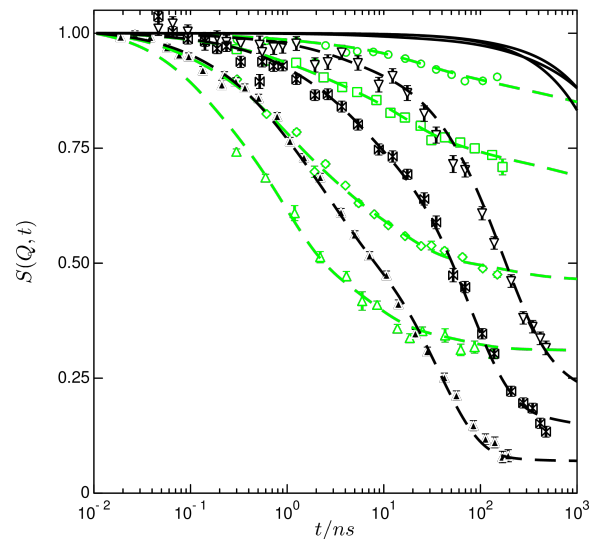


Figure 6. Same data and model (symbols and dashed lines) as in figure 5 but the computed curves (solid black lines) pertain to a slowed down matrix dynamics.

The transition from a more or less close representation of the short chain ($S_1(Q, t)$) to that of the long chain ($S_2(Q, t) = S_c(Q, t)$) visibility is illustrated in figure 1 of ref. [1]. Where the plateau visibility steadily increases with increasing concentration ϕ_{tracer} , thereby continuously evolving towards the long chain scattering function for 90%+ concentration. However, note again that this only pertains the visibility, the increased mobility of long chains diluted by a large amount of small tracers is not included and must be modelled into $S_2^0(Q, t)$ of the long chains. If on the other hand a small amount of the long chains are labelled $S_2(Q, t)$ and the rest of long chains $S_c(Q, t)$ and the short chains $S_1(Q, t)$ have the background scattering length density (typically by using deuterated components) the effect on the scattering can be found in figure 2 of ref. [1]. The long chain visibility here is less affected by the short chain presence, still some minor reduction of the observed plateau levels are encountered. But again these curves shown are rather hypothetically since the computations completely ignores the effect of dilution by short chains on the "pure" dynamic structure functions $S_{2,c}^0(Q, t)$ of the long chains (and vice versa). The determination of these influences, which probably would be the

goal of an experiment then can be obtained by (model) fitting of the "pure" structure functions $S_{1,2,c}^0(Q, t)$ that enter the dynamic RPA procedure. To serve as tool enabling this in an easy and practically feasible way is the main purpose of the dynamic RPA procedure presented.

6 Conclusion

Interpretation of experiments aiming at the dynamics of a labelled component in a polymer mixture requires special attention if the dynamic properties of the various components are different. Due to the partial visibility of the non-labelled (background, matrix) component in the scattering signal, their different dynamics may modify the characteristic times and/or shapes of the observed relaxation curves. Applying dynamic RPA to the mixture allows to compute this mutual influence. Practical application is made accessible by implementing a procedure that yields the RPA-corrected scattering functions from the "pure" scattering function data (from any kind of modelling). This procedure can be included into the model computation during fitting and thus determine the proper model parameters (model values) of the "pure" scattering functions of labelled components. The Fortran implementation of this procedure is available see ref. [1]. While there is no effect for mixtures of dynamically equal polymers (i.e. the conventional h/d-mixtures used to create contrast in SANS and NSE-experiments) different dynamics as in the example of small diffusing chains in a matrix of reptating slow long chains [12] huge distortions are observed and would lead to erroneous conclusions if the RPA-effect is not properly accounted for. But also in dynamically less different mixtures mutual influence on relaxation rates will occur with possibly worse consequences for the conclusion if their not so obvious influence remains unnoticed.

References

- [1] M. Monkenbusch, M. Kruteva, M. Zamponi, L. Willner, I. Hoffman, B. Farago, D. Richter, *Journal of Chemical Physics* **152**, 054901 (2020)
- [2] B. Hammouda, *Advances in Polymer Science* **106**, 87 (1993)
- [3] H. Frielinghaus, *Colloid and Polymer Science* **299**, 1031 (2021)
- [4] Y. Melnichenko, G. Wignall, D. Schwahn, *Fluid Phase Equilibria* **212**, 209 (2003), 16th European Conference on Thermophysical Properties, Imperial Coll, London, England, Sep 01-04, 2002
- [5] A. Akcasu, M. Benmouna, H. Benoit, *Polymer* **27**, 1935 (1986)
- [6] M. Tombakoglu, A. Akcasu, *Polymer* **33**, 1127 (1992)
- [7] A. Akcasu, R. Klein, B. Hammouda, *Macromolecules* **26**, 4136 (1993)
- [8] I. Erukhimovich, Y. Kudryavtsev, *European Physical Journal E* **11**, 349 (2003)
- [9] S. Mochrie, *Macromolecules* **36**, 5013 (2003)
- [10] D. Lumma, S. Mochrie, *Macromolecules* **34**, 8303 (2001)
- [11] A. Akcasu, M. Tombakoglu, *Macromolecules* **23**, 607 (1990)
- [12] M. Zamponi, M. Kruteva, M. Monkenbusch, L. Willner, A. Wischnewski, I. Hoffmann, D. Richter, *Physical Review Letters* **126**, 187801 (2021)
- [13] M. Kruteva, M. Zamponi, I. Hoffmann, J. Allgaier, M. Monkenbusch, D. Richter, *Macromolecules* **54**, 11384 (2021)