Structural properties of a fluid of polymers confined in a porous matrix of star polymers

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Abstract. We have studied the structural properties of a fluid of linear polymer chains under the external field of a disordered porous matrix, represented by a frozen liquid configuration of star polymer particles. To this end, and using a coarse-grained description of both fluid and matrix, we have applied the replica Ornstein-Zernike formalism to this particular case where soft and ultra-soft inter-particle potentials have come into play. Our systematic investigations point out how the matrix influences the structural properties of the confined polymer fluid.

1 Introduction

Theoretical and experimental investigations have recently revealed new and unexpected phenomena in the dynamic behaviour of binary mixtures of soft fluids (see, e.g., [1–3] and references therein). This refers in particular to the glass-formation scenario: for instance, evidence was found in a binary mixture of arrested star polymers and mobile linear homopolymers that a re-melting process can be induced by increasing the amount of chain polymers whereas a re-vitrification of the ergodic fluid results by increasing the chains' size [1]. Another striking example are binary star polymer mixtures of different size and functionality where the authors report about two distinctly different glass states that occur depending on the system parameters [2]. These findings strongly suggest that hitherto unknown and unexpected types of arrested states and kinetic phase diagram topologies will be unveiled in future investigations.

While glass-formation in one-component soft systems is quite well understood within mode coupling theory (MCT) [3,4], the situation is considerably more complex in binary systems. Here, there is evidence that glass-formation can occur independently for the two components. Therefore one is faced with a large variety of possible scenarios, that range from a binary, equilibrated mixture, over systems where one component has vitrified while the other is still fluid, to systems where both components are glasses. Over the past, the amount of theoretical tools available to study the various scenarios was based, essentially, on the one- and two-component versions of MCT. Recently, a new theoretical development of the MCT-formalism offered a new possibility to look into these questions from a complementary point of view. The new scheme successfully combines two appropriate concepts [5]: MCT for the glass formation with the replica formalism for fluids [6] that are confined in disordered (and possibly glass-like) porous media.

We have chosen a simpler approach, where we explicitly assume that one component of the mixture has already vitrified (its translational degrees of freedom are frozen) while the other one is still in the fluid phase. From the comparison of the correlation functions of this system with a fully equilibrated (and possibly supercooled) binary mixture, we draw conclusions

of the influence of a disordered (glass-like) matrix on the structure of the fluid. To this end we have applied for the first time the replica formalism [6] that was originally proposed for atomic fluids to systems governed by soft and ultra-soft interactions. In this concept the double averaging procedure (one over the fluid particles for a fixed matrix, the other over all possible matrix representations) is carried out explicitly, leading to the replica Ornstein-Zernike (ROZ) equations [6] that relate the correlation functions that describe the entire system.

The particular system we have chosen is the one investigated in [1], namely a mixture of star polymers and linear polymer chains. Using model potentials for both components we obtain from the solution of the ROZ equations (in combination with the hypernetted chain (HNC) closure relation [7]) information about the structure of the two species.

2 Model and theory

We consider a quenched-annealed (QA) system where the porous matrix (quenched component) is formed by the structure of a frozen liquid configuration of star polymer particles. A fluid of linear polymer chains (annealed component) is then immersed into this matrix. Again following [1] and introducing the indices '0' for the matrix and '1' for the fluid we adopt the following interparticle potentials between the two species at a temperature T [with $\beta = (k_B T)^{-1}$]:

$$\beta \Phi_{00}(r) = \frac{5}{18} f_0^{3/2} \begin{cases} -\log\left(\dfrac{r}{\sigma_0}\right) + \dfrac{1}{1 + \sqrt{f_0}/2} & r \leq \sigma_0 \\[3mm] \dfrac{\sigma_0}{r\left(1 + \sqrt{f_0}/2\right)} \exp\left[-\dfrac{\sqrt{f_0}}{2\sigma_0}(r - \sigma_0)\right] & r > \sigma_0, \end{cases} \tag{2.1}$$

$$\beta \Phi_{01}(r) = \alpha(r/\xi)^{-12}, \qquad \beta \Phi_{11}(r) = \varepsilon \exp[-(r/\sigma_1)^2], \tag{2.2}$$

where, σ_0 and σ_1 are the characteristic lengths of the star-star [8] and chain-chain [9] interactions, respectively. The functionality parameter f_0 stands for the number of arms of the star polymers. α and ε are energy parameters, which are fixed to the following values: $\alpha = 1.3$, $\varepsilon = 1.87 \, k_B T$, according to reference [1]. Following [1] we chose $\sigma_0 = 64 \, \text{nm}$ and use this quantity in the following as the unit length. Finally, $\xi = d/2 + R_g^{lin}$, $d = \sigma_0(1 + 2/\sqrt{f_0})$ being the diameter of a star polymer, when considered as a dense sphere and R_g^{lin} being the gyration radius of the linear polymer chain. Our system is characterized by $f_0 = 263$ and $q = \sigma_1/\sigma_0 = 0.3$ (see Figure 2). Finally, we introduce the partial number densities ρ_0 and ρ_1.

The structural properties of the system are described by the corresponding correlation functions, which are related via the ROZ equations [6]:

$$\begin{aligned} h_{00} &= c_{00} + \rho_0 c_{00} \otimes h_{00} \\ h_{10} &= c_{10} + \rho_0 c_{10} \otimes h_{00} + \rho_1 c_{11} \otimes h_{10} - \rho_1 c_b \otimes h_{10} \\ h_{11} &= c_{11} + \rho_0 c_{10} \otimes h_{10} + \rho_1 c_{11} \otimes h_{11} - \rho_1 c_b \otimes h_b \\ h_b &= c_b + \rho_0 c_{10} \otimes h_{10} + \rho_1 c_{11} \otimes h_b + \rho_1 c_b \otimes h_{11} - 2\rho_1 c_b \otimes h_b, \end{aligned} \tag{2.3}$$

where the symbol $\otimes$ between two functions represents their convolution. The $h_{ij}(r)$ and the $c_{ij}(r)$ for $i,j = 0,1$ are the total and direct correlation functions. The formalism [6] also defines so-called blocking functions $h_b(r)$ and $c_b(r)$: the fluid-fluid correlation function $h_{11}(r)$ can be split according to $h_{11}(r) = h_c(r) + h_b(r)$, the $h_c(r)$ being the so-called connected part and $h_b(r)$ the blocking part. They provide information how the correlations between the fluid particles are realized (for details see [6]).

These integral-equations have to be solved along with a suitable set of closure relations [10], where we have used the hypernetted chain approximation [7], i.e., $h_{ij}(r) = \exp[-\beta \Phi_{ij}(r) + h_{ij}(r) - c_{ij}(r)]$; the indices can assume the values '0', '1', and 'b'. In the latter case, by definition $\Phi_b(r) = 0$ [6]. Our choice for this particular closure is motivated by the fact that the HNC approximation is known to provide reliable results for soft fluids [11].

3 Results and discussion

In Figure 1 we show the fluid-fluid distribution functions and their blocking part of the QA system at a fixed matrix density $\rho_0\sigma_0^3 = 0.35$ and four different fluid densities ($\rho_1\sigma_1^3 = 0.05$, 0.15, 0.2, and 0.3). We also show the corresponding distribution functions of the fully equilibrated (EQ) binary mixture. For the $g_{11}(r)$ of the QA system we observe the characteristic features of a soft system. The short-range correlation hole, usual for steeply repulsive systems, is suppressed and the fact that the main peaks of the $g_{11}(r)$ are located at short distances indicates that the external, repulsive field of the matrix forces the fluid particles to overlap or even to sit on top of each other. Since on the other side the fluid particles repel each other as well they have to find within the limited space left free by the matrix an energetic compromise: while at small densities they can still form a distinct second layer around each fluid particle (see the side maximum at $r/\sigma_1 \sim 1.0$) this possibility is completely suppressed at higher densities; the side-maximum has now mutated to a shoulder and particles are rather forced to sit on top of each other. The next layer is found only at a distance of $\sim 6r/\sigma_1$. Looking at the blocking part we observe that the region where $g_b(r)$ coincides with $g_{11}(r)$ becomes smaller as the density is increased. Following the interpretation of $g_b(r)$ [6] this means that more and more correlations between fluid particles of different pores are mediated rather via the matrix particles than via the fluid particles. The EQ mixture shows a qualitatively similar, but quantitatively different behaviour from the QA case.

In Figure 2 we display the matrix-matrix distribution function ($\rho_1\sigma_1^3 = 0$) and compare them with the $g_{00}(r)$ of the EQ mixture. With increasing ρ_1 we observe a shift in the main peak of $g_{00}(r)$ and a concomitant lowering of its value; in addition, a pronounced double peak structure gradually evolves. Viewing the chain polymers as depleting agents they induce via
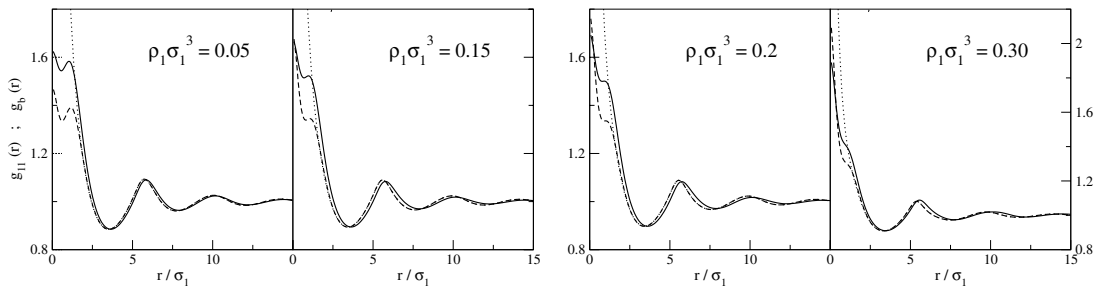
Fig. 1. Blocking part, $g_b(r)$ (dotted line) and fluid-fluid distribution functions, $g_{11}(r)$ for the QA system (solid line), compared to the $g_{11}(r)$ in the EQ system (dashed line). The density of the matrix and of the larger component is fixed ($\rho_0\sigma_0^3 = 0.35$). Four fluid densities (insets) have been considered.
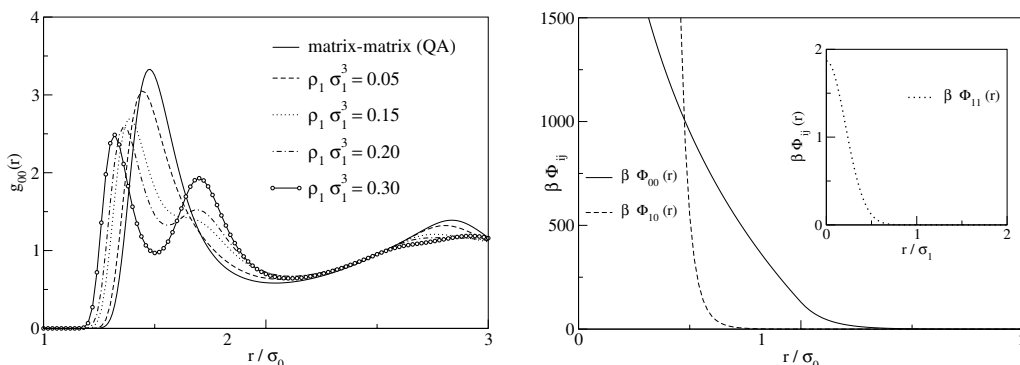
Fig. 2. Left: Matrix-matrix distribution function of the QA system and $g_{00}(r)$ of the EQ system. **Right**: All interaction potentials characterizing the binary (QA and EQ) system.

their repulsion an attractive depletion force between the star polymers which cause the shift in the peak of $g_{00}(r)$. As ρ_1 is further increased space becomes scarce; the only way to escape this restriction is that the stars start to overlap leading to the double peak structure. Evidently, the depletion mechanism is not at work in the QA-case, as the big stars are not free to escape their cages and experience the effective attractions mediated by the smaller polymers. This readily explains also the differences between the QA- and EQ-functions $g_{11}(r)$ shown in Figure 1: in the EQ-case, they result from the common equilibration of stars and chains, whereas in the QA-case they represent the response of the mobile component to an inert (and random) external field.

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