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2007 J. Phys.: Condens. Matter 19 205144

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Anomalous relaxation in binary mixtures: a dynamic facilitation picture

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Received 2 January 2007

Published 25 April 2007

Online at stacks.iop.org/JPhysCM/19/205144

Abstract

Recent computational investigations of polymeric and non-polymeric binary mixtures have reported anomalous relaxation features when both components exhibit very different mobilities. Anomalous relaxation is characterized by sublinear power-law behaviour for mean-squared displacements, logarithmic decay in dynamic correlators, and a striking concave-to-convex crossover in the latter by tuning the relevant control parameter, in analogy with predictions of the mode-coupling theory for state points close to higher-order transitions. We present Monte Carlo simulations on a coarse-grained model for relaxation in binary mixtures. The liquid structure is substituted by a three-dimensional array of cells. A spin variable is assigned to each cell, representing unexcited and excited local states of a mobility field. Changes in local mobility (spin flip) are permitted according to kinetic constraints determined by the mobilities of the neighbouring cells. We introduce two types of cell ('fast' and 'slow') with very different rates for spin flip. This coarse-grained model qualitatively reproduces the mentioned anomalous relaxation features observed for real binary mixtures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Binary mixtures of small and large particles with sufficiently large size disparity, at low or moderate concentrations of the small particles, exhibit a large separation in the timescales for both components. Recent computational investigations of polymeric and non-polymeric mixtures of soft spheres [1–3] in such conditions have reported anomalous relaxation features at intermediate intervals, extending in time over more than three decades between the short-time ballistic and long-time diffusive regimes. These anomalous features are: (i) sublinear

power-law behaviour for mean-squared displacements, with decreasing exponent on decreasing the temperature, (ii) logarithmic relaxation in dynamic correlators, (iii) concave-to-convex crossover in dynamic correlators by tuning the relevant control parameter. These results exhibit striking analogies with predictions of the mode-coupling theory (MCT) for state points close to higher-order MCT transitions [4–6], which arise in regions of the control parameter space where competition between different mechanisms for dynamic arrest takes place. For the fast component in binary mixtures we have suggested a competition between confinement and bulk-like caging [1–3], respectively induced by the host matrix formed by the slow component, and by the surrounding particles belonging to the fast component. This view is supported by the observed non-trivial analogies [3] with a recent MCT theory for fluids confined in matrices with interconnected voids [7, 8], for which a higher-order point has been explicitly derived. Striking analogies with anomalous relaxation features in short-ranged attractive colloids are also observed. For these latter systems a higher-order MCT transition has been derived as the result of a competition between steric repulsion and reversible bond formation for dynamic arrest [6, 9–11].

Kinetically constrained models [12, 13] are used as coarse-grained pictures for relaxation in supercooled liquids. In these models, the liquid structure is substituted by an array of cells. The cell size roughly corresponds to a density correlation length. A spin variable is assigned to each cell, with values 0 or 1 denoting respectively unexcited and excited local states in a mobility field. Changes in local mobility (spin flips) for a given cell are permitted according to kinetic constraints determined by the mobilities of the neighbouring cells. Propagation of mobility, which yields structural relaxation, occurs via dynamic facilitation: microscopic regions become temporarily mobile only if neighbouring regions are mobile. Kinetically constrained models provide in a simple way an important feature exhibited by glass-forming liquids: the growing of dynamic correlation lengths by decreasing temperature, leading to dynamic heterogeneity [14–17].

Some of the anomalous dynamic features exhibited by short-ranged attractive colloids, and associated with a higher-order point within the framework of MCT, such as logarithmic relaxation or reentrant behaviour of the diffusivity [6], have been recently reproduced by a simple model based on dynamic facilitation [18]. Motivated by this fact and by the mentioned dynamic analogies with binary mixtures, we investigate a simple kinetically constrained model aimed at reproducing qualitative relaxation features for such mixtures. In section 2 we introduce the model and give computational details. Simulation results are presented and discussed in section 3.

2. Model and computational details

We have carried out Monte Carlo (MC) simulations on a variation [19] (see below) of the north-or-east-or-front (NEF) model recently investigated by Berthier and Garrahan [17]. In this three-dimensional model, directionality in the kinetic constraints is imposed to mimic fragile liquid behaviour [17]. Spin flip of a given cell is only permitted if there is at least one excited neighbouring cell in the north-or-east-or-front direction. More specifically, if the cell is denoted by its position vector $\mathbf{i} = (i_x, i_y, i_z)$, spin flip is permitted according to the following rules.

- (i) At least one of the neighbouring cells in the north $(i_x, i_y, i_z + 1)$, or east $(i_x, i_y + 1, i_z)$, or front $(i_x + 1, i_y, i_z)$ direction is excited, i.e., it has spin 1.
- (ii) If (i) is fulfilled, spin flip is accepted according to the Metropolis rule [20]. Hence, $1 \rightarrow 0$ is always accepted, while $0 \rightarrow 1$ is accepted with a thermal probability $[1 + \exp(1/T)]^{-1}$, where T is the temperature.

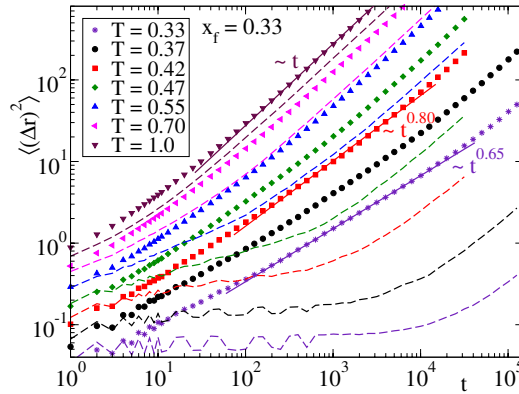


Figure 1. Temperature dependence of the mean-squared displacement at composition $x_f = 0.33$. Symbols correspond to fast cells. Dashed lines correspond to slow cells (same temperatures as for the former ones, decreasing from top to bottom). Solid straight lines indicate linear or sublinear power-law behaviour (exponents are given).

In the present work we investigate a binary mixture of cells with the same population of excitations, $[1 + \exp(1/T)]^{-1}$, but different rates for excitation, $\exp(-E/T)[1 + \exp(1/T)]^{-1}$, and decay, $\exp(-E/T)$, of the cell mobility. This choice fulfils detailed balance. We use the activation energies $E = 0$ and 3 for the different components, which are respectively denoted as ‘fast’ and ‘slow’ cells. Hence, the spin flip rules for the fast component are the same as in the original NEF model, aimed at reproducing bulk-like dynamics. The probability of spin flip for the slow cells is decreased by a factor $\exp(-3/T)$ as compared to that of the fast cells, providing a large timescale separation for relaxation of both components (see below).

The mixture composition, x_f , is defined as the fraction of fast cells. We investigate a wide range of composition and temperature as control parameters. A square box of side $N = 50$ cells is used. Periodic boundary conditions are implemented. Slow and fast cells are randomly distributed according to the selected value of x_f . Time is given in MC steps. Within each MC step a total of N^3 trials (one trial for each cell) is performed. The configuration of the mobility field at times t and $t + 1$ is defined as that respectively before and after the N^3 trials.

3. Results and discussion

We have evaluated the mean-squared displacement according to the definition given in [21]. A ‘probe molecule’ placed in a given cell \mathbf{i} at time t is permitted to perform a jump $\Delta = (\Delta_x, \Delta_y, \Delta_z)$, with $\Delta_\alpha \in \{-1, 0, 1\}$, to an adjacent cell $\mathbf{j} = \mathbf{i} + \Delta$ provided that *both* \mathbf{i} and \mathbf{j} are instantaneously (i.e., at the same time t) in an excited state. Otherwise the jump is not permitted. If in the former case there are several candidates amongst the adjacent cells; one of them is randomly selected. The mean-squared displacement is computed from an average over the trajectories of different (non-interacting) probes initially placed in different cells. In the case of the binary mixture investigated in this work, only jumps between cells of a same component (‘fast’ \rightarrow ‘fast’ or ‘slow’ \rightarrow ‘slow’) are permitted. In this way the motion of a probe initially placed in a cell of a given component remains coupled to the mobility field of that component. Figure 1 shows, at a fixed composition $x_f = 0.33$, results for the mean-squared displacement computed according to this procedure. The short-time ballistic regime exhibited by real systems is obviously absent, due to the coarse-grained character of the model. A large timescale separation is induced between both components at low temperatures. In analogy with

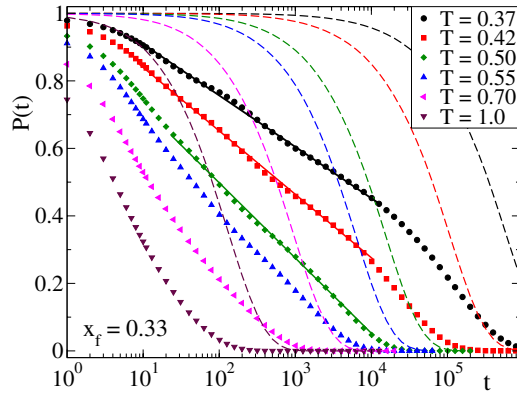


Figure 2. Temperature dependence of the mean persistence function $P(t)$ at composition $x_f = 0.33$. Symbols correspond to fast cells. Dashed lines correspond to slow cells (same temperatures as for the former ones, decreasing from left to right). Solid straight lines indicate logarithmic relaxation.

the behaviour displayed by binary mixtures with large size disparity [1–3], an intermediate sublinear power-law behaviour is observed for the fast component, and the corresponding exponent decreases on decreasing the temperature. The latter takes a value of about 0.6 at the lowest investigated temperature.

We have also computed the mean persistence function $P(t) = \sum_i p(\mathbf{i}; t)/N^3$, where $p(\mathbf{i}; t)$ is the persistence function of the cell \mathbf{i} at time t . The latter takes the value 1 if no spin flip has occurred for that cell in the interval $[0, t]$. If one or more spin flips have occurred, it takes the value 0. According to the picture of dynamic facilitation, the decay of $P(t)$ is a signature of structural relaxation [17]. Figure 2 shows the temperature dependence of $P(t)$ at composition $x_f = 0.33$. The first decay usually observed for any correlator in real systems—corresponding to the transient regime at microscopic times—is again absent due to coarse-graining. As for the mean-squared displacement, the introduction of very different rates for cell spin flip yields very different relaxation times for fast and slow cells. While slow cells display standard relaxation, fast cells exhibit rather different relaxation features. In full analogy with results for dynamic correlators of the fast component in binary mixtures [1–3], $P(t)$ shows a concave-to-convex crossover on decreasing the temperature. At an intermediate temperature, pure logarithmic relaxation is observed over a time interval of nearly three decades. This behaviour is also observed by fixing the temperature and varying the mixture composition (see figure 3).

It is worthy of remark that the features displayed in figures 2 and 3 are not specific to $P(t)$. Qualitatively analogous results are exhibited by other dynamic correlators, such as intermediate scattering functions. An example is displayed in figure 4 for the incoherent correlator $F_s(q, t)$. Following the definition given in [22], the latter is computed, for a wavevector \mathbf{q} , as $F_s(q, t) = \langle \exp[i\mathbf{q} \cdot (\mathbf{r}(t) - \mathbf{r}(0))] \rangle$, where \mathbf{r} is the position of a probe molecule. The latter is permitted to jump between adjacent cells according to the same rules imposed for the evaluation of the mean-squared displacement of each component (see above). The brackets denote an average over initial locations of the probe. As in the case of the mean persistence function, $F_s(q, t)$ exhibits a concave-to-convex crossover on decreasing the temperature, and a logarithmic decay at some intermediate state point.

In summary, the highly non-trivial anomalous relaxation features recently reported for binary mixtures with a large timescale separation between both components can be qualitatively reproduced by a simple kinetically constrained model. The fact that recent work within this

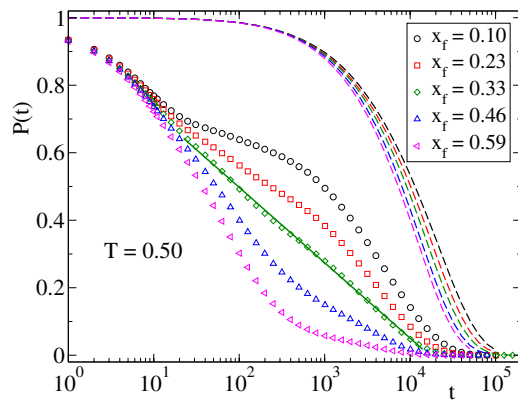


Figure 3. Symbols: composition dependence of $P(t)$, at $T = 0.50$, for the fast cells. Dashed lines correspond to slow cells (same compositions as for the former ones, decreasing from left to right). The solid straight line indicates logarithmic relaxation.

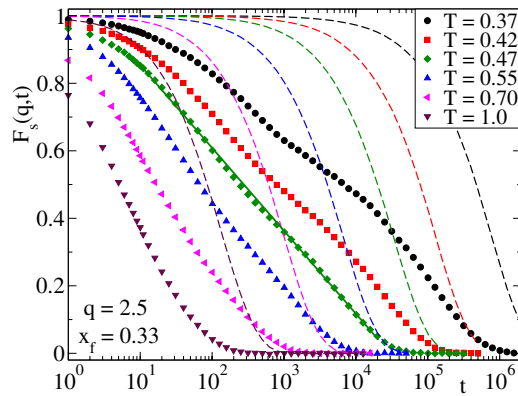


Figure 4. Temperature dependence of $F_s(q, t)$, at composition $x_f = 0.33$ and wavevector $q = 2.5$. Symbols correspond to fast cells. Dashed lines correspond to slow cells (same temperatures as for the former ones, decreasing from left to right). The solid straight line indicates logarithmic relaxation.

approach [18] also reproduces unusual relaxation features for short-ranged attractive colloids suggests that dynamic facilitation is a relevant ingredient for relaxation in systems with several competing mechanisms for dynamic arrest. Results reported here provide a new step in extending the picture of dynamic facilitation, which had been used basically for describing bulk-like relaxation, to more complex situations.

Acknowledgments

We thank J P Garrahan and L Berthier for useful discussions.

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