Physics Letters A 378 (2014) 3567–3571

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

A toy MCT model for multiple glass transitions: Double swallow tail singularity

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ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form 3 October 2014
Accepted 6 October 2014
Available online 8 October 2014
Communicated by V.M. Agranovich

Keywords:
Disordered systems
Mode Coupling Theory
Liquid–glass transition
Multiple glasses

ABSTRACT

We propose a toy model to describe in the frame of Mode Coupling Theory multiple glass transitions. The model is based on the postulated simple form for static structure factor as a sum of two delta-functions. This form makes it possible to solve the MCT equations in almost analytical way. The phase diagram is governed by two swallow tails resulting from two A_4 singularities and includes liquid–glass transition and multiple glasses. The diagram has much in common with those of binary and quasibinary systems.

A large number of papers studying the liquid–glass transition have been published during last decades. They include results of real experiments, computer simulations and various theoretical approaches. Nowadays, the most popular and the most cited of the various theories of glasses are based on the mean-field replica approach [1] and the so-called Random First Order Transition theory (RFOT) [2–4], both based on analogies with the well-developed equilibrium statistical mechanics of spin glasses. However, numerous results were obtained in the framework of the Mode Coupling Theory (MCT) (see, e.g., the pioneering work [5], the reviews [6,7], and also a detailed presentation in the recent monograph [8]). The most important drawback of mean-field dynamics and MCT is that the MCT transition it describes is not observed in real materials. MCT cannot be used to describe viscosity data close to the experimental glass transition T_g, since it does not even predict thermally activated behavior. Worse, MCT predicts a transition at which the system freezes completely: not only a fraction of the density fluctuations get frozen but also self-diffusion gets arrested [9]. Although now the investigations of dynamical heterogeneities (see e.g. [4,10]) in glassy systems favor the modifications of MCT, one can affirm that it was for a long time the only consistent theory describing details of the transitions in supercooled liquids. It is now recognized that the MCT transition must be interpreted as an approximate theory of a crossover taking place in the dynamics. In the present paper we remain in the framework of the traditional MCT.

The MCT was first used to describe the transition to the glass state in the system with the hard-core potential in [5] and then in a large number of various systems. Its applicability was confirmed experimentally and in computer simulations (see [6–8,11]). A major achievement of MCT is the possibility to apply the same formalism to different materials and theoretical models, basically starting from the microscopic interactions between atoms and molecules. At the same time, papers where the possibility of describing the glass–glass transition for certain potentials in the MCT framework have recently appeared: in this case, the glass characterized by the nonergodicity parameter $f_q^{(1)}$ transforms into another glass with the nonergodicity parameter $f_q^{(2)}$. Such a transition was predicted for systems with a potential consisting of a solid core and a very narrow and deep attractive well [12–15]. In this case, at high temperatures the first glass state is determined by repulsion as for the system of hard spheres, while the second glass state exists at low temperatures and is determined by attraction. It is the competition between these two states that determines the glass–glass transition. The glass–glass transition line continues the low-temperature liquid–glass transition line smoothly to the glass region and ends at a third-order bifurcation point [12–15]. It was shown that A_4 singularity [16–18] usually accompanies the glass–glass transition [19,20].

Another class of systems with two characteristic length and, so, with the possibility of glass–glass transition is presented by binary and quasibinary systems. Mixtures of hard spheres are commonly used as simple model systems with slow dynamics avoiding crystallization. Binary hard spheres were considered in the frame of MCT approach in a number of papers (see, e.g. [21–23]) and

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http://dx.doi.org/10.1016/j.physleta.2014.10.009
0375-9601/© 2014 Published by Elsevier B.V.

phase diagrams containing multiple glasses were obtained. Now, a quasibinary system of hard spheres with an additional repulsive step in the potential (so-called square-shoulder, or collapsing spheres system) is also in the focus of interest. This system and its smoothed versions were widely studied [24–29]. It was shown that a series of unusual phenomena are observed in the system. MCT approach to this system was used in [30–33] exploiting different approaches for the static structure factor. The MCT equations reveal the A_4 bifurcation singularities and A_3 end points indicating glass–glass transitions.

In the present paper, we propose a toy model aiming to describe in the frame of MCT approach the main common features of the phase diagrams of binary and quasibinary systems in the simplest way. We postulate a very simple form of static structure factor (SSF) as a sum of two delta-functions. This enables us to obtain results in almost analytical way. We do not consider our SSF as an approximate one for any given system, so we do not claim to obtain a quantitative description of some concrete system. Our phase diagram is given as a function of characteristics of our toy SSF rather than real physical parameters. Nevertheless we are going to obtain a qualitative phase diagram with the same topology and the same characteristics of glasses as in the mentioned MCT papers. In fact, one can easily see the similarity of the phase diagram presented in this paper and that obtained in the most detailed paper [23] for the case of the real binary hard sphere system which is in correspondence with the experiments on colloidal suspensions [34,35]. In our simple model it occurs to be possible to trace the multiplication of singularities and the appearance of a double swallow tail.

In MCT, the system dynamics is described in terms of the autocorrelation function of the density fluctuations $\Phi_q(t) = \langle\rho_q(t)\rho_{-q}(0)\rangle/\langle\rho_q(0)\rho_{-q}(0)\rangle$ well known in the theory of liquids (see, e.g., Ref. [36]). Here, $\rho_q(t)$ is the Fourier transform of the system density. The autocorrelation function satisfies the equation

$$\frac{\partial^2\Phi_q(t)}{\partial t^2} + \nu_q\frac{\partial\Phi_q(t)}{\partial t} + \Omega_q^2\Phi_q(t) + \Omega_q^2\int_0^t dt' m_q(t-t')\frac{\partial\Phi_q(t')}{\partial t'} = 0, \tag{1}$$

where ν_q corresponds to white noise and Ω_q is the characteristic frequency. The memory function $m_q(t)$ has the form

$$m_q(t) = \frac{1}{2}\int\frac{d^3k}{(2\pi)^3}V_{\vec{q},\vec{k}}\Phi_{\vec{k}}(t)\Phi_{\vec{q}-\vec{k}}(t). \tag{2}$$

The interaction potential of the system particles is included in the vertex function,

$$V_{q,k} = \rho S_{\vec{q}}S_{\vec{k}}S_{\vec{q}-\vec{k}}\left[\vec{q}\vec{k}c_k + \vec{q}(\vec{q}-\vec{k})c_{\vec{q}-\vec{k}}\right]^2/q^4 \tag{3}$$

through the static structure factor S_q of the liquid and the direct correlation function c_q [36]. These two quantities are related:

$$S_q = 1/(1-\rho c_q). \tag{4}$$

The behavior of the solution of Eq. (1) at large times determines relaxation processes in the system [8]. As $t\to\infty$, the algebraic equation for the limit correlation function $f_q = \Phi_q(\infty)$:

$$\frac{f_q}{1-f_q} = \frac{1}{2}\int\frac{d^3k}{(2\pi)^3}V_{\vec{q},\vec{k}}f_{\vec{k}}f_{\vec{q}-\vec{k}} \tag{5}$$

can be obtained from Eq. (1). Eq. (5) always has the trivial solution $f_q = 0$ corresponding to the liquid (ergodic) phase. Eq. (5) can also have a nonzero solution $f_q > 0$ corresponding to a nonergodic glass phase. The value f_q can be regarded as an order parameter (or a nonergodicity parameter) for the liquid–glass transition.

Now we introduce the following toy model – the oversimplified form of SSF which enables us to advance farther in analytical way:

$$S(q) \approx 1 + A\delta(q-k_1) + B\delta(q-k_2). \tag{6}$$

Our model SSF contains two maxima at k_1 and k_2 with the area A and B under the maxima. An example of such SSF can be found in Ref. [32].

After substituting of (6) in Eqs. (3)–(5) it is easy to see that the function f_q as a function of q is nonzero only in two points: k_1 and k_2. So, with no other approximations we obtain the following system of two nonlinear algebraic equations for two nonergodicity parameters $f_1 \equiv f_{k_1}$ and $f_2 \equiv f_{k_2}$ (compare Ref. [5]):

$$\frac{f_1}{1-f_1} = (af_1 + bf_2)^2[=F_1],$$
$$\frac{f_2}{1-f_2} = x(af_1 + bf_2)^2[=F_2], \tag{7}$$

where three control parameters are

$$x = \frac{S(k_2)}{S(k_1)}\frac{k_2^2}{k_1^2}, \tag{8}$$

$$a = \frac{S(k_1)k_1}{8\pi^2\rho}, \tag{9}$$

$$b = \frac{S(k_2)k_2}{8\pi^2\rho}. \tag{10}$$

Let us note that Eqs. (7)–(10) were derived in the paper [32] where SSF in the form (6) was first used as a rough approximation for the case of square-shoulder system. However, in [32] we did not pay attention to the symmetry of the equations we are dealing with now.

Our goal is to obtain the points $\{x, a, b\}$ where the solutions of Eqs. (7) become multiple. So, we now pass directly to the problem of finding the bifurcation points of Eqs. (7). As is well known (see, e.g. [37]), the uniqueness of a solution of two functional equations,

$$\chi_1(z_1, z_2) = 0; \qquad \chi_2(z_1, z_2) = 0$$

does not hold at the points where the determinant of derivatives $\det\frac{\partial\chi_i}{\partial z_k}$ is zero.

Let us note, first, that the character of nonlinearity of Eqs. (7) is so, that one can expect the bifurcation singularities up to fourth order (A_4). This singularity corresponds to the division of the space of three control parameters into three parts by the surface of the figure called "swallow tail" (see [16–18]). These parts correspond, respectively, to the absence of nontrivial solution of the equations, to the part with two solutions, and to the remaining part with four solutions. Second, the equations possess a kind of a symmetry and of a degeneracy, both having a physical ground contented in the form of SSF. The duplication of the singularities demonstrates one of the consequences of these properties – we obtain "double swallow tail".

In fact, it is easy to see that Eqs. (7) are invariant under the transformation:

$$f_1 \to f_2'; \qquad f_2 \to f_1'$$
$$a \to \sqrt{x'}b'; \qquad b \to \sqrt{x'}a'; \qquad x \to 1/x'.$$

This means that for every solution of (7) there exists another one. The same is true for every bifurcation singularity point A_k ($k = 2, 3, 4$).

At the bifurcation points we have $\det[\delta_{qk} - A_{qk}] = 0$, where