Mode coupling theory for the glass transition in a simple binary mixture

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Abstract. The mode coupling equations describing the ideal glass transition in simple liquids are generalised to treat binary mixtures. These equations are solved numerically to obtain the phase diagram, the glass order parameters, and the exponents ruling the long time dynamics of a soft sphere model for which numerical simulation results are available.

1. Introduction

The mode coupling theory (MCT) of the glass transition [1, 2] developed in the past few years provides a detailed picture of the microscopic dynamics in supercooled liquids: in its simplest version, the MCT describes the glass transition as a bifurcation from ergodic to non-ergodic behaviour below a critical temperature T_c. Near T_c, the dynamics of the liquid ($T > T_c$) and of the glass ($T < T_c$) for mesoscopic times is predicted to obey scaling laws with non-universal (system dependent) exponents. These predictions have been used to analyse experimental data for several systems (fused salts, organic and polymeric glasses) yielding at least a qualitative agreement [3–6]. However, MCT applies strictly speaking only to simple liquids, for which the available data on the glass transition come exclusively from numerical simulations. MCT has in particular been used to study the glass transition in hard spheres [2, 7] and Lennard-Jones [8, 9] systems. The numerical simulation of the glass transition in such one-component systems is, however, plagued by the phenomenon of crystalline nucleation, which makes the very long runs needed for a precise characterisation of the transition impossible. In this paper, we shall apply MCT to a simple binary mixture for which this phenomenon can be avoided [10]; this model has been extensively studied [10–14] by molecular dynamics (MD) simulations, and its glass transition has been well characterised [13, 14]. It consists of a mixture of soft spheres with different diameters interacting via an inverse power potential:

$$v_{ij}(r) = \varepsilon(\sigma_{ij}/r)^{12} \tag{1}$$

where $i, j = 1, 2$ refer to the different species and the diameters are additive, i.e. $\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$. We shall be particularly interested in the case studied in [13, 14], i.e. an equimolar mixture ($x_1 = x_2 = 0.5$) with $\sigma_{22} = 1.2$.

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Due to the scaling properties of the potential (1), the thermodynamic state of the mixture can be characterised by two parameters only: we shall use here the composition $x = N_2/N$ and the reduced coupling parameter which includes the effect of both the temperature T and the density n [10]:

$$\Gamma = n\sigma_{\text{eff}}^3 (\varepsilon/k_{\text{B}}T)^{1/4} \tag{2}$$

with $\sigma_{\text{eff}}^3 = x_1^2\sigma_{11}^3 + 2x_1x_2\sigma_{12}^3 + x_2^2\sigma_{22}^3$. In the following section, we present the generalisation of the mode coupling equations to binary mixtures. Numerical results for the soft spheres model are described in section 3.

2. Mode coupling equations for binary mixtures

Like in the one-component case [2], the MCT focuses on the relaxation of density fluctuations; these fluctuations are now described for each wavevector q by a 2×2 matrix $\mathbf{F}(q, t)$, with matrix elements $F_{ij}(q, t) = (1/N)\langle\rho_i^*(q, t)\rho_j(q, 0)\rangle$, $\rho_i(q, t)$ referring to the Fourier components of the density. For $t = 0$, $\mathbf{F}$ reduces to the structure factor matrix $\mathbf{S}(q)$. The time evolution of $\mathbf{F}$ is described by the generalised Langevin equation [15]

$$\ddot{\mathbf{F}}(q, t) + \mathbf{\Omega}^2(q)\mathbf{F}(q, t) + \int_0^t \mathrm{d}s\, \mathbf{M}(q, t - s)\dot{\mathbf{F}}(q, s) = 0 \tag{3}$$

where

$$\Omega_{ij}^2(q) = q^2 k_{\text{B}}T(x_i/m_i)\delta_{ik}[\mathbf{S}^{-1}]_{kj}(q)$$

(summation over repeated indexes is implicit throughout the paper).

The memory matrix $\mathbf{M}$ is separated into a regular term which is irrelevant here and a mode coupling term describing the decay of density fluctuations into pairs of them, quadratic in the F_{ij}. This term reads explicitly:

$$M_{ij}^{\text{MC}}(q, t) = \frac{k_{\text{B}}T}{16\pi^3 nx_jm_i} \int \mathrm{d}k\, V_{i\varepsilon\eta}(q, k)V_{j\varepsilon'\eta'}(q, k)F_{\varepsilon\varepsilon'}(k, t)F_{\eta\eta'}(q - k, t) \tag{4}$$

where

$$V_{i\varepsilon\eta}(q, k) = (q - k)\cdot(q/q)\delta_{i\varepsilon}c_{i\eta}(q - k) + k\cdot(q/q)\delta_{i\eta}c_{i\varepsilon}(k) + x_iqc_{i\varepsilon\eta}^{(3)}(k, q - k) \tag{5}$$

and the direct correlation functions c_{ij} are given by

$$c_{ij}(q) = \delta_{ij}/x_i - [\mathbf{S}^{-1}(q)]_{ij}. \tag{6}$$

In the liquid state, $\mathbf{F}(q, t = +\infty) = 0$, i.e. one has an ergodic behaviour. The ideal glass transition corresponds to the possibility of a non-zero limit for $\mathbf{F}(q, t)$, $\mathbf{F}(q)$, for infinite times. If such a limit exists, equations (2) and (4) yield

$$\mathbf{F}(q) = (1/q^2)\mathbf{S}(q)\mathbf{N}(q)\,(\mathbf{S}(q) - \mathbf{F}(q)) \tag{7}$$

with

$$N_{ij}(q) = (m_i/x_ik_{\text{B}}T)M_{ij}^{\text{MC}}(q, t = \infty). \tag{8}$$

This non-linear equation can be solved iteratively in order to obtain the frozen form

factors (or non-ergodicity parameters) $F_{ij}(q)$, i.e. the order parameter for the glass transition.

Equation (7) has two important properties: first of all, it can be shown that when the two species are identical, its resolution is equivalent to solving simultaneously the equations for the total density and the tagged particle density correlators given in [2]. The second and most important property is that (7) is independent of the particle masses (this follows trivially from (4) and (8)). This means that the bifurcation from ergodic to non-ergodic behaviour depends only on static quantities like the structure factors. The particle masses influence only the short-time dynamics, but not the value of the critical density or of the exponents determining the long-time behaviour.

The general properties of (7) have been studied in detail in [16] for a one-component system. This analysis can be extended to the mixture case with the following results. The non-ergodicity parameters are obtained by solving iteratively

$$\mathbf{F}^{(n+1)}(q) = [q^2\mathbf{I} + \mathbf{S}(q)\mathbf{N}_q(\mathbf{F}^{(n)}, \mathbf{F}^{(n)})]^{-1}\mathbf{S}(q)\mathbf{N}_q(\mathbf{F}^{(n)}, \mathbf{F}^{(n)})\mathbf{S}(q) \tag{9}$$

where the quadratic dependence of $\mathbf{N}(q)$ on $\mathbf{F}$ has been explicitly indicated. The convergence of these iterations is ruled by the spectrum of a stability matrix $\mathbf{C}$, which can be defined through its action on a vector $\delta F = (\delta F_{11}(q), \delta F_{12}(q), \delta F_{22}(q))$

$$(\mathbf{C}\delta F)_q = (1/q^2)(\mathbf{S}_q - \mathbf{F}_q)(\mathbf{N}_q(F, \delta F) + \mathbf{N}_q(\delta F, F))(\mathbf{S}_q - \mathbf{F}_q) \tag{10}$$

(in this formula and the following one, the dependence on q has been indicated only by a subscript).

Unlike in the one-component case [17], no *a priori* statement can so far be made concerning the spectrum of the operator $\mathbf{C}$. However, our numerical calculations do not show any difference between this and the one-component case. We must therefore consider the existence of a non-degenerate largest eigenvalue for $\mathbf{C}$, E_0, whose approach to unity when the coupling is decreased yields the transition point. The scenario for the transition is then very similar to the one-component case: for large couplings, $(\Gamma > \Gamma_c)$, $0 < E_0 < 1$ and the iteration (9) converges to a stable fixed point with $\mathbf{F}(q) \neq 0$. The transition point is characterised by E_0 approaching unity according to

$$(1 - E_0)^2 = A_0\varepsilon + \mathrm{O}(\varepsilon^2) \tag{11}$$

with $\varepsilon = (\Gamma - \Gamma_c)/\Gamma_c$. If H_q is an eigenvector of $\mathbf{C}$ associated with E_0, the non-ergodicity parameter near Γ_c behaves according to

$$\mathbf{F}_q = \mathbf{F}_q^c + A_1\varepsilon^{1/2}\mathbf{H}_q^c. \tag{12}$$

Finally, the time evolution of the correlators in the β-relaxation region is determined by the exponent parameter λ:

$$\lambda = \left(\int_0^\infty \mathrm{d}q\, q^{-2}[(\mathbf{S}_q - \mathbf{F}_q^c)\mathbf{N}_q(H^c, H^c)(\mathbf{S}_q - \mathbf{F}_q^c)]_{ij}\hat{H}_{ij}(q)\right)\Big/$$

$$\times \left(\int_0^\infty \mathrm{d}q\, [H_q(\mathbf{S}_q - \mathbf{F}_q^c)^{-1}H_q]_{ij}\hat{H}_{ij}(q)\right). \tag{13}$$
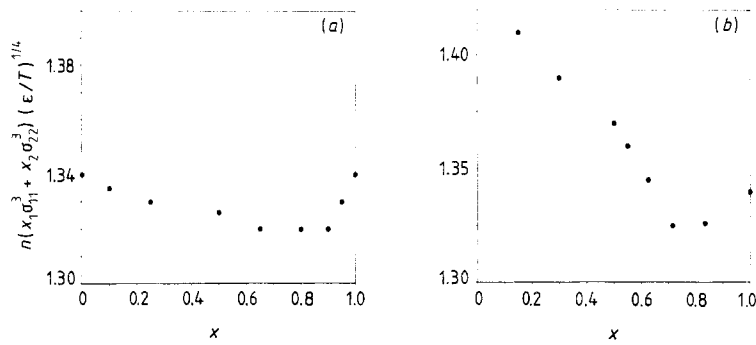
Figure 1. (*a*) The variation of the critical density with composition for a fixed diameter ratio $(\sigma_2/\sigma_1 = 1.2)$. The points indicate the reduced glass transition density $n(x_1\sigma_{11}^3 + x_2\sigma_{22}^3)$ $(\varepsilon/T)^{1/4}$ for various concentrations. (*b*) The variation of the critical density with the diameter ratio for a fixed concentration $(x_2 = 0.5)$.

$\hat{H}_q$ is an eigenvector of the transposed operator **C** associated with the eigenvalue E_0. From λ one obtains two exponents $a, b, 0 < a < 1/2, 0 < b < 1$:

$$\Gamma(1 - a)^2/\Gamma(1 - 2a) = \lambda = \Gamma(1 + b)^2/\Gamma(1 + 2b).$$

The β-relaxation occurs on a time scale ω_ε^{-1}, with $\omega_\varepsilon \simeq \varepsilon^{1/2a}$. On this scale, the correlators behave according to

$$\mathbf{F}_q(t) = \mathbf{F}_q^c(t) + \varepsilon^{1/2}\mathbf{H}_q f_\pm(\omega_\varepsilon t) \qquad \varepsilon \to 0\pm. \tag{14}$$

For larger times, $\omega_\varepsilon^{-1} \ll t \ll (\omega_\varepsilon')^{-1}$, with $\omega_\varepsilon' \simeq \varepsilon^\gamma, \gamma = 1/2a + 1/2b$ one enters the α-relaxation regime in the liquid, while the structure remains frozen in the glass. The exponent γ characterises the divergence predicted for the transport coefficients when the transition is approached from the liquid side.

All these properties follow directly from [16, 17], to which the reader is referred for a detailed discussion. Finally, the equations that determine the long-time limits for the tagged particle density correlators (i.e. the Lamb–Mössbauer factors) can be found in [18].

3. Numerical results for soft spheres mixtures

We have solved equations (7) and (13) for several values of the parameters characterising the mixture (composition and diameter ratio). If the triplet correlations are neglected (a reasonable approximation in view of the results of [7]), the only necessary inputs are the structure factors. These were calculated using the Rogers–Young integral equations [19], which have been shown to reproduce very accurately the simulation results [10].

Figures 1(*a*) and (*b*) show respectively the phase diagrams obtained by varying the concentration for a fixed diameter ratio $(\sigma_2/\sigma_1 = 1.2)$ and for a fixed concentration $(x_2 = 0.5$, equimolar mixture) with a variable diameter ratio. The ordinate axis is in both cases $n(x_1\sigma_{11}^3 + x_2\sigma_{22}^3)(\varepsilon/T)^{1/4}$, so identical values are obtained for $x = 1$ (pure big spheres) and $x = 0$ (small spheres) in figure 1(*a*). From figure 1(*a*) the reduced critical density is seen to be fairly insensitive to the composition. A stronger variation is observed in figure 1(*b*), which shows in particular the destabilising influence of the small spheres on the
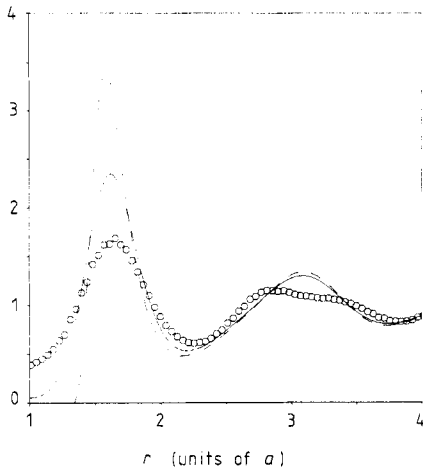
Figure 2. The pair correlation function $g_{11}(r)$ (broken curve) and the non-ergodicity parameter $F_{11}(r)$ (full curve) calculated at the transition point ($\Gamma = 1.32$) for $\sigma_2/\sigma_1 = 1.2$, $x_2 = 0.5$. Dots: simulation results from [14] for $F_{11}(r)$ at the transition point ($\Gamma = 1.46$). r is given in units of the mean interparticle distance, $a = (3/4\pi\rho)^{1/3}$.

glassy structure [18]. The case of a very small diameter ratio ($\sigma_1/\sigma_2 < 0.15$) yields specific problems which have been considered in [18] and will not be discussed here.

The various quantities defined in section 2 (form factors $\mathbf{F}(q)$, exponent parameter λ, eigenvector $\mathbf{H}(q)$ and the corresponding spatial Fourier transforms $\mathbf{F}(r)$ and $\mathbf{H}(r)$) have been calculated for different concentrations and diameter ratios. The results appear to be quite insensitive to these parameters, so in the following we shall restrict ourselves to the case $\sigma_2/\sigma_1 = 1.2$, $x_2 = x_1 = 0.5$. Moreover, they are qualitatively very similar to the results obtained in [7] for a one-component hard sphere system, to which the reader is referred for a more detailed discussion. For these parameters, the glass transition is predicted to occur for a coupling $\Gamma = 1.32$. As usual [7, 8], this value underestimates the simulation result $\Gamma = 1.46$ [13, 14] by about 10% in density. Such an underestimate can be expected from the basic assumptions of the simple MCT used here, which strongly restricts the possible decay channels for density fluctuations. The error is not dramatically large, but it will restrict our comparison with simulation results to qualitative aspects.

The exponent parameter λ is found to be $\lambda = 0.73$, yielding exponents $a = 0.31$, $b = 0.59$, $\gamma = 2.46$. The power law curves fitted to the simulation results [12, 14] usually yield $\gamma \simeq 2$, but the difference can hardly be considered significant in view of the rather restricted range of the data [7]. Note that the value of λ is very close to the results obtained for the one-component systems [7, 9] or for other diameter ratios (e.g. $\lambda = 0.72$ for $\sigma_1/\sigma_2 = 0.55$, $\lambda = 0.67$ for $\sigma_1/\sigma_2 = 0.15$). More interesting is the general aspect of the non-ergodicity parameter in r-space, $\mathbf{F}(r)$, illustrated on figure 2 for the matrix element F_{11} at the transition point. $\mathbf{F}(r)$ characterises the frozen structure of the glass. It is clear from figure 2 that the MCT overestimates this structure, the reasons for this discrepancy being, most probably, the same as those that yield an underestimate of the critical density. However, qualitative features of $\mathbf{F}(r)$ are correctly reproduced: in particular, the oscillations are in phase with those of $g(r)$ and the two functions differ only on a rather restricted range (two to three neighbour shells). This feature is illustrated by the plot of $H_{11}(r)$ (figure 3), whose range characterises the spatial extent of the β-relaxation (14) (see [7]).

Finally, figure 4 shows the number–number and concentration–concentration form factors, normalised by their $t = 0$ value, i.e. $F_{NN}(q)/S_{NN}(q)$ and $F_{CC}(q)/S_{CC}(q)$. Since the diameter ratio is close to 1, it seems reasonable to assume (in the spirit of the
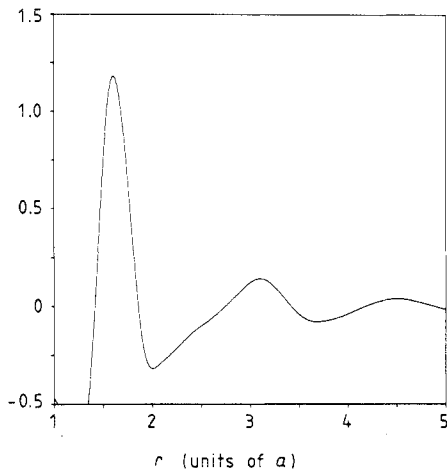
Figure 3. The eigenvector $H_{11}(r)$ of the stability matrix **C** at the transition point.
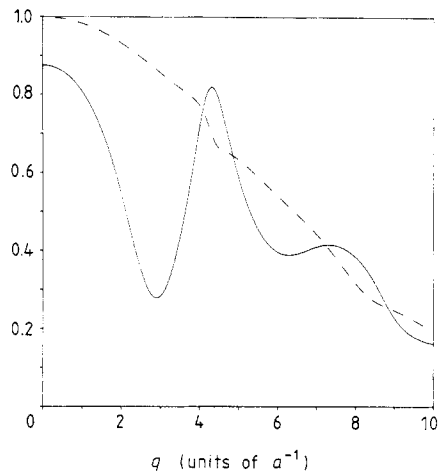
Figure 4. The normalised non-ergodicity parameters $F_{NN}(q)/S_{NN}(q)$ and $F_{CC}(q)/S_{CC}(q)$ for number–number (full curve) and concentration–concentration (broken curve) fluctuations in Fourier space (q is in units of a^{-1}, where a is the mean interparticle distance).

simplified model of [1, 2] and of the effective liquid representation of [10]) that the transition is driven by the number–number correlations with wavevector q_0 which occurs at the peak of S_{NN}. The conclusions of [20] thus suggest that the time relaxation of the small-q concentration (or charge) fluctuations, which do not decrease much below their $t = 0$ value, could have a spectrum presenting a β-relaxation peak.

4. Conclusions

We have investigated the predictions of a simple mode coupling theory for the glass transition of a simple binary alloy. An important prediction of the theory is that the transition point and the associated critical behaviour are independent of the mass ratio between the two species. This is in agreement with the numerical simulation results [10, 14] and indicates that the glass transition, though a dynamical one (in the sense that it corresponds to a divergence in transport coefficients), originates purely in equilibrium properties of the liquid. The agreement of MCT with the molecular dynamics results is reasonable, the origin of the discrepancy being qualitatively understood [21]. It should be noted that the properties investigated here (critical density, the influence of the mass ratio and the ergodicity parameters) are quite different and complementary to the predictions that have been compared previously to neutron scattering data [3]. Further numerical simulations would be useful in order to test the scaling laws predicted by MCT near the glass transition, in particular in the β-relaxation region.

Acknowledgments

References

[1] Leutheusser E 1984 *Phys. Rev.* A **29** 2765
[2] Bengtzelius U, Götze W and Sjölander A 1984 *J. Phys. C: Solid State Phys.* **17** 5915
[3] Götze W and Sjögren L 1988 *Proc. ILL Workshop on Dynamics of Disordered Materials (Grenoble, 1988)* (Berlin: Springer) p 18
[4] Knaak K, Mezei F and Farago B 1988 *Europhys. Lett.* **4** 921
[5] Fujara F and Petry W 1988 *Europhys. Lett.* **4** 921
[6] Frick B, Richter D, Petry W and Buchenau U 1988 *Z. Phys.* B **70** 73
[7] Barrat J L, Götze W and Latz A 1989 *J. Phys.: Condens. Matter* **1** 7163
[8] Bengtzelius U 1986 *Phys. Rev.* A **33** 3433
[9] Bengtzelius U 1986 *Phys. Rev.* A **34** 5059
[10] Bernu B, Hansen J P, Hiwatari Y and Pastore G 1987 *Phys. Rev.* A **36** 4891
[11] Mountain R and Thirumalai D 1987 *Phys. Rev.* A **36** 3300
[12] Pastore G, Bernu B, Hansen J P and Hiwatari Y 1988 *Phys. Rev.* A **38** 454
[13] Barrat J L, Roux J N, Hansen J P and Klein M L 1988 *Europhys. Lett.* **7** 707
[14] Roux J N, Barrat J L and Hansen J P 1989 *J. Phys.: Condens. Matter* **1** 7171
[15] Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)
[16] Götze W 1985 *Z. Phys.* B **60** 195
[17] Götze W 1987 *Amorphous and Liquid Metals* ed E Lüscher *et al* (Dordrecht: Martinus Nijhoff) p 34
[18] Bosse J and Thakur J S 1987 *Phys. Rev. Lett.* **998** 59
[19] Rogers F J and Young D A 1984 *Phys. Rev.* A **30** 999
[20] Götze W and Sjögren L 1989 *J. Phys.: Condens. Matter* **1** 4203
[21] Götze W and Sjögren L 1987 *Z. Phys.* B **65** 415