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The mode-coupling theory of liquid-to-glass transitions

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Abstract. A mode-coupling theory for supercooled liquid dynamics exhibits bifurcation singularities which cause a temperature T_c for the crossover from liquid to glass behaviour. Near T_c the long-time relaxation is a two-step process related to the experimentally known α- and β-relaxation in structural glass formers. The dynamical anomalies predicted by the theory for the two processes are reviewed.

The mode-coupling theory (MCT) of glassy dynamics is based on closed equations of motion for a set of M correlators $\phi_q(t)$, $q = 1, \ldots, M$. A first equation connects accelerations, Hooke's restoring forces and friction forces

$$\ddot{\phi}_q(t) + \Omega_q^2 \phi_q(t) + \int_0^t M_q(t-t')\, \dot{\phi}_q(t')\; \mathrm{d}t' = 0\,. \tag{1a}$$

The generalized viscosity or polarization kernel M relates a force at time t to velocities at times $t' \leq t$. The kernel M is expressed in terms of a Newtonian friction constant ν_q and two kernels m_q and δ_q via an equation which is algebraic for the Fourier-transformed variables

$$M_q(\omega) = [\mathrm{i}\nu_q + m_q(\omega)]/\{1 - \delta_q(\omega)[\mathrm{i}\nu_q + m_q(\omega)]\}\,. \tag{1b}$$

The frequencies Ω_q, ν_q determine the short time transient motion. Kernels m_q and δ_q are given in terms of the correlators via mode-coupling functionals

$$m_q(t) = \mathcal{F}_q(\boldsymbol{V}, \phi_k(t)) = \sum_k v_{q,k}^{(1)}\, \phi_k(t) + \sum_{kp} v_{q,kp}^{(2)}\, \phi_k(t)\, \phi_p(t) + \cdots\,. \tag{2a}$$

$$\delta_q(t) = \sum_k w_{q,k}^{(1)}\, \ddot{\phi}_k(t) + \sum_{kp} w_{q,kp}^{(2)}\, \ddot{\phi}_k(t)\, \phi_p(t) + \cdots\,. \tag{2b}$$

The non-negative coefficients of these polynomials, the coupling constants of the model, are combined to the state vector $\boldsymbol{X} = (\boldsymbol{V}, \boldsymbol{W})$ in the control parameter space $\mathbb{R}$. In applications q refers e.g. to the wavevector modulus of density fluctuations so that $\phi_q(t) = \langle \rho_{\boldsymbol{q}}^*(t) \rho_{\boldsymbol{q}} \rangle / S_q$, $S_q = \langle |\rho_{\boldsymbol{q}}|^2 \rangle$ is the density correlator. Its spectrum determines the dynamical structure factor $S(q,\omega) = S_q \phi_q''(\omega)$. Coupling to transversal currents [1] is not noted above for the sake of simplicity. For the models with $\boldsymbol{W} = 0$ one can show, that (1) and (2) has a unique solution with $\phi_q''(\omega) \geq 0$, [2].

The space $\mathbb{R}$ can be split into the open set of liquid states $\mathcal{D}_\mathrm{L}$, the set of ideal glass states $\mathcal{D}_\mathrm{G}$, and the set of glass transition singularities $\mathcal{D}_C$. $\mathcal{D}_\mathrm{L}$ contains the weak coupling region $\boldsymbol{X} \sim (\boldsymbol{0},\boldsymbol{0})$. For $\boldsymbol{X} \in \mathcal{D}_\mathrm{L}$ the correlations decay to zero $\phi_q(t \to \infty) = 0$ and the spectra $\phi_q''(\omega)$ depend smoothly on ω. The set $\mathcal{D}_\mathrm{G}$ consists of certain points $\boldsymbol{X} = (\boldsymbol{V},\boldsymbol{0})$ where $f_q(\boldsymbol{V}) = \phi_q(t \to \infty)$ is positive and regular in $\boldsymbol{V}$; $\mathcal{D}_\mathrm{G}$ contains the points with $\mathcal{F}_q(\boldsymbol{V},1) > V_0$ with some $V_0 > 0$ [3,4]. $f_q(V)$ obeys the equation $f_q/(1-f_q) = \mathcal{F}_q(\boldsymbol{V}, f_k)$ [3,5]; if this equation has several solutions, the largest one is $f_q(\boldsymbol{V})$ [6]. $f_q(\boldsymbol{V}) > 0$ is the signature of ideal glass states [7]. Like for a crystalline solid the dynamical structure factor exhibits an elastic line on top of a continuum

$$\boldsymbol{X} \in \mathcal{D}_\mathrm{G} : S(q,\omega) = S_q \pi f_q \delta(\omega) + \text{continuum}. \tag{3}$$

Unlike in a crystal, the Debye–Waller factor f_q here is positive for all q. The singularities of $f_q(\boldsymbol{V})$ for $\boldsymbol{V} \in \mathcal{D}_C$, the glass transition singularities [1], are the bifurcation points of the model. The transition points from $\mathcal{D}_\mathrm{L}$ to $\mathcal{D}_\mathrm{G}$, the ideal liquid-to-glass transitions, are special glass transition singularities. The bifurcations at $\boldsymbol{V}_\mathrm{c}$ are of the cuspoid type A_l, $l = 2,3,\ldots$ [8,9]. In the limit $\boldsymbol{V} \to \boldsymbol{V}_\mathrm{c}$ one can solve (1) and (2) asymptotically for $t/t_0 \gg 1$. Near an A_3 singularity one finds e.g. [10]: $\phi_q(t) - f_q(V^c) = h_q p(\ln(t/t_0),\, g_2,\, g_3)$. Here p is the Weierstrass elliptic function with moduli $g_{2,3}$ depending smoothly on $\boldsymbol{V}$. Depending on $\boldsymbol{V} - \boldsymbol{V}_\mathrm{c}$ this implies e.g.

$$p \sim 1/\ln^2(t/t_0) \qquad \ln(t/t_0) \qquad (t_0/t)^a \qquad -(t/\tau)^b\,. \tag{4}$$

The exponents a and b depend smoothly on $\boldsymbol{V}$ and they approach zero for $g_{2,3} \to 0$. The MCT is interesting for two reasons. First, it describes new bifurcation scenarios with a variety of non-trivial relaxation laws. The novel features are caused by the interplay of the retardation effects in (1*a*) with the nonlinearities. Second, the decay laws near $\boldsymbol{V}_\mathrm{c} \in \mathcal{D}_\mathrm{c}$ exhibit stretching; and this is the most important feature of glassy dynamics. The simplest singularities are degenerate A_2 points where $f_q(V_\mathrm{c}) = 0$. They are of relevance for percolation transitions [11–13] and orientational glass transitions [14]. The combination of degenerate A_2 and A_3 singularities is of interest for spin glass transitions [8, 10, 15]. In the following only the canonical Whitney fold singularity A_2 will be considered, which was proposed for the description of structural glass transitions [5, 16].

For simple liquids the MCT can be derived from first principles [1, 5] by exploiting Kawasaki's factorization approximation [17] to fluctuating force correlations, which appear e.g. in the formally exact generalized kinetic equation approach [18]. One gets only $v^{(2)}$ and $w^{(2)}$ terms in (2*a*) and (2*b*). Linear terms $v^{(1)}$, $w^{(1)}$ appear if models with frozen disorder are considered [11–15]. Kernel m describes relaxation with streaming patterns of incompressible backflow, the dominant dynamical feature of dense fluids [19]. Equations (1) and (2) with $\delta = \nu = 0$ extend the Feynman–Cohen approach of this phenomenon [20]. The term δ describes the other essential relaxation mechanism of dense systems: phonon assisted particle hopping over free energy barriers. If applied to disordered electron systems, (1) and (2) reproduce the standard results [21]. For large m, the dominance of kernel δ in (1*b*) leads to the Arrhenius law for the relaxation rate [22], the experimental signature of activated transport. If hopping is ignored, lowering the temperature T or increasing the density n drives the system through an ideal liquid-to-glass transition at T_c or n_c. Due to $\delta_q(T_c) \neq 0$ the system remains in a liquid state throughout [1, 23]. If $\delta(T_c)$ is not too large the dynamics for $T \sim T_c$ exhibits strong anomalies reflecting the existence of the singularity V_c. So a crossover from liquid to glass dynamics for T near T_c is described by the MCT. The known dynamical anomalies of the liquid state appear as glass transition precursors. For $T \to T_c$ and $\delta(T_c) \to 0$ the $\boldsymbol{V}_c$ anomalies can be calculated to some extend analytically. The critical values T_c, n_c have been calculated for the hard-sphere system [5], for the Lennard-Jones system [24] and for hard-sphere [25] and soft-sphere mixtures [26]. For other systems, T_c can be identified by measuring the predicted crossover phenomena and fitting the data to the theoretical formulae.

The relaxation near an A_2 singularity is a two-step process characterized by two time scales τ_α, τ_β. The long-time part for $\tau_\beta \ll t$ is called α-process; it leads to the α-peaks of the susceptibility spectra $\chi''(\omega) \propto \omega\phi''(\omega)$. The peak position can be chosen to define $1/\tau_\alpha$. The β- process describes the dynamics outside the microscopic transient before the center of the α-process for $t_0 \ll t \ll \tau_\alpha$. For an idealized transition both times diverge: τ_α, $\tau_\beta \to \infty$ for $T \to T_c+$. But τ_α/τ_β diverges also for $T \to T_c+$ so that the time interval $\tau_\beta \ll t \ll \tau_\alpha$, where both processes overlap, becomes large near the transition. Hopping processes, $\delta(T_c) \neq 0$, prevent τ_α, τ_β to diverge and cause crossovers to large but finite values $\tau_\alpha(T_c) \gg \tau_\beta(T_c) \gg t_0$ [1, 27].

The Debye–Waller factor of the ideal glass is the α peak area for $T < T_c$ [1, 27]. It shows a square root singularity as function of the separation parameter $\sigma \propto (T_c - T) \propto n - n_c$ for $T \to T_c-$ [3]

$$f_q = f_q^c + h_q A\sqrt{\sigma}\,. \tag{5}$$

For $T > T_c$ the α-relaxation part obeys the α-scaling law [4]

$$\phi_q(t) = F_q(t/\tau_\alpha)\,. \tag{6}$$

Here the master function F depends smoothly on $\boldsymbol{V}$, so that the strong T or n dependence is caused by the scale τ_α only. There is α-scale universality [4] in the following sense for $T > T_c$. The scales for two α- processes, say τ_α^1 for the viscosity and τ_α^2 for the dielectric loss, increase strongly but $\tau_\alpha^1/\tau_\alpha^2$ is only a smooth function of T. Scale universality and scaling law (6) are usually invalid for $T < T_c$. The short-on-scale-τ_α decay process follows the von Schweidler fractal law [3, 28]

$$F_q(t/\tau_\alpha) = f_q^c - h_q(t/\tau_\alpha)^b + \mathrm{O}\big((t/\tau_\alpha)^{2b}\big) \tag{7}$$

where the exponent $0 < b \leq 1$ is the same for all correlations for the same system. For a variety of examples, $F_q(\tilde{t})$ is very close to the Kohlrausch law $F_K(\tilde{t}) = f_q^c \exp(-\tilde{t}^\beta)$ [29–33]. This law is a mere fitting formula: the exponent β, as opposed to b, has no physical meaning. β is different for different quantities [33], it depends, for example, on the wavevector [30]. The equation for master function F_q [4] is complicated and does not allow for simple solutions. The many known experimental examples, where F differs strongly from F_K, can be modelled by the MCT. The α-resonances make it desirable to extend the hydrodynamic description of the long-wavelength fluctuations in supercooled liquids. This can be done by extending (1) and (2) somewhat [34, 35].

Within the β-region the correlations can be factorized [3]

$$\phi_q(t) = f_q^c + h_q\mathcal{G}_\sigma(t) \tag{8}$$

so that the problem of solving (1,2) is reduced to determine the single correlator $\mathcal{G}_\sigma(t)$; this holds for all A_l singularities and reflects the centre manifold theorem for bifurcations. The β-scaling law holds, which implies that the σ-dependence of $\mathcal{G}_\sigma$ is given by the correlation scale $C_\sigma = \sqrt{|\sigma|}$, the time scale τ_β, and the σ-independent master function $g_\pm$

$$\mathcal{G}_\sigma(t) = C_\sigma g_\pm(t/\tau_\beta) \qquad \sigma \lessgtr 0\,. \tag{9}$$

For large on-scale-τ_β times one gets $g_+(\hat{t} \gg 1) = \text{const}$, implying (5) and $g_-(\hat{t} \gg 1) = -B\hat{t}^b$, implying (7). For short on-scale-τ_β times critical decay, specified by a fractal exponent $0 < a < 0.4$, is obtained [3, 28]

$$\phi_q(t) = f_q^c + h_q(t_0/t)^a + \mathrm{O}\big((t_0/t)^{2a}\big)\,. \tag{10}$$

A special implication of this decay is the β-peak phenomenon for which one finds asymptotically the Cole–Cole law [9, 33]. The β-dynamics reflects the topology of the A_2 singularity and this leads to the following universality. All details of the MCT condense to the time scale t_0 and the exponent parameter $\frac{1}{2} \le \lambda < 1$. Both depend smoothly on $\boldsymbol{V}$. The latter fixes the master function $g_\pm$, in particular the exponents a, b [3, 28]. The most transparent form for the scaling equation [28] reads [36]

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_0^t g_\pm(t-t')g_\pm(t')\,\mathrm{d}t' - \lambda g_\pm(t)^2 = \pm 1 \qquad \sigma \lessgtr 0\,. \tag{11}$$

The equation can be generalized to account for hopping, whereby $\mathcal{G}$ obeys a two parameter scaling law [1]. The anomalous dimensionalities a, b also rule the two scales [1]. If δ can be neglected one gets [3, 28]

$$\tau_\beta = t_0/|\sigma|^{1/2a} \qquad \tau_\alpha = \tau_\beta/|\sigma|^{1/2b}\,. \tag{12}$$

Since the mode-coupling functional (2a) is given solely by the structure factor S_q [5], master functions F_q, g, in particular the exponents a and b and also f_q, h_q are determined by S_q. The whole dynamics, except for the scale t_0, merely reflects equilibrium thermodynamics as given by the potential landscape in configuration space [9]. The fractal spectra reflect cantor sets for waiting time distributions [37]. For the hard-sphere system [5, 38] and for a soft-sphere mixture [26] f_q, h_q and λ have been calculated. In more complicated cases λ has to be used so far as a fitting parameter in the analysis of data.

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