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Mode-coupling theory for translational and orientational dynamics near the ideal glass transition

R Schilling

Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, D-55099 Mainz, Germany

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Abstract. We briefly review the molecular mode-coupling theory which takes into account both the translational and the orientational degrees of freedom. Depending on the symmetry of the physical system, several scenarios of ideal glass transition from ergodic to nonergodic behaviour may occur. The validity of the scaling laws for the α - and β -relaxation, originally derived from mode-coupling theory for simple liquids, will be discussed. These predictions will be compared with results from molecular dynamics simulations. We will demonstrate which of the predictions are consistent with these numerical results and which are not. Particular attention will be given to the rotational diffusion tensor.

1. Introduction

Despite considerable efforts during recent years the structural glass transition is still not completely understood. Several theoretical approaches exist which describe some aspects of that transition more or less satisfactorily.

There is the mode-coupling theory (MCT) which has contributed most to this subject. In its original, *idealized* version it provides a closed set of nonlinear integro-differential equations for the *dynamical* structure factor $S(q, t)$ of a *simple* liquid in *equilibrium* [1]. MCT is a *microscopic* theory in the sense that its solution is completely determined by the knowledge of the *static* structure factor $S(q)$ which, in principle, can be calculated from the microscopic interactions by means of statistical mechanics. The main result of (idealized) MCT is a *dynamical* transition at a critical temperature T_c (or critical density n_c) from an ergodic to a nonergodic phase, i.e. from a liquid to an ideal glass. In the vicinity (above and below) of T_c , MCT makes several interesting predictions where the existence of a so-called β -relaxation timescale (not to be confused with the Johari–Goldstein β -peak) t_σ is probably the most important one. There are several papers which review MCT and its predictions (see e.g. [2–5]). The test of the predictions has been a great challenge for computational and experimental physicists. Clear indications of the existence of T_c have been provided for several glass-forming systems, although the transition is *not* sharp. Many numerical and experimental results are consistent with various MCT predictions. Such tests of MCT were reviewed, e.g. in references [3, 6, 7]. The absence of a sharp transition is consistent with the *extended* MCT [8, 9] which also takes into account the coupling to current density. In physical terms this coupling introduces hopping processes which restore ergodicity, at least on a very long timescale.

Quite a different approach has recently been suggested which is called the replica theory (RT) for structural glasses (see e.g. [10–14] and the contribution by Mezard and Parisi in

this Special Issue [30]). This approach is based on the observation that the time-dependent configuration remains in the vicinity of a reference configuration in the case of a glassy phase but not for a liquid. RT predicts a *static* glass transition at a temperature T_f at which the configurational entropy per particle vanishes. Accordingly T_f , which is below T_c , can be identified with the Kauzmann temperature. Since RT starts from a microscopic Hamiltonian it can be considered as a microscopic theory, as well. First numerical investigations give some evidence for the existence of T_f [11, 13, 14].

For mean-field-type spin-glass models with p -spin interactions ($p \geq 3$) for which MCT becomes exact (see e.g. reference [15]), both the dynamical and the static transition are sharp. In recent years it has been speculated that structural glasses have much in common with such spin-glass models. However, it remains to be shown that this is really true for structural glass formers with short-range interactions and without quenched disorder. As regards T_c for (idealized) MCT, we already know that in general no sharp transition occurs at T_c . Whether in such systems a sharp static transition exists at T_f has not been proven. In addition, compared to the tests of MCT, there are only few numerical tests and no experimental one of RT.

Although it is not our purpose to give a complete overview of all existing theoretical approaches to the structural glass transition, we would like to mention the facilitated kinetic Ising model and its variants which are designed to model the important phenomenon of cooperativity in a supercooled liquid (see e.g. the contribution by Jäckle *et al* in this Special Issue [31]), the use of an energy landscape description (see Angelani *et al*, Biroli *et al*, Dasgupta *et al* and Ritort in this Special Issue [32]) and instantaneous normal-mode analysis (see Cavagna *et al* in this Special Issue [33]).

Our contribution will focus on the extension of MCT for simple liquids to molecular systems. This is important because (i) most glass formers are of molecular origin and (ii) it will offer the possibility of investigating the freezing of the orientational degrees of freedom and the role of their coupling to the translational ones. After giving a concise review of molecular mode-coupling theory (MMCT), we will elucidate in a first part similarities of and differences between the general predictions of MCT and MMCT. This will address the question of several glass transition scenarios for the freezing of translational and orientational modes and the validity of both scaling laws for α - and β -relaxation. In a second part we will review the first numerical tests of MMCT for a supercooled liquid of diatomic molecules. Most attention will be devoted to the rotational diffusion tensor which MMCT predicts to become zero at the ideal glass transition temperature T_c . On the other hand, simple physical arguments will be presented showing that this cannot happen. Although an orientational cage prevents the relaxation to equilibrium of the molecular orientations it does not imply vanishing of the rotational diffusion constant.

2. Molecular mode-coupling theory

2.1. Molecular mode-coupling equations

In this subsection we briefly review the extension of MCT to molecular liquids. This has been done for a linear molecule in a simple liquid [16], for a molecular liquid of linear molecules [17] and for general molecules [18, 19] by use of a molecular representation, i.e. decomposing the degrees of freedom for a rigid molecule into translational and orientational ones. Recently, a site-site representation has also been used [20]. For more details on molecular mode-coupling theory (MMCT) the reader may consult references [16–19].

The starting point of MMCT are the microscopic, tensorial density modes:

$$\rho_\kappa(\vec{q}, t) = i^\ell (2\ell + 1)^{c1/2} \sum_{j=1}^N e^{i\vec{q} \cdot \vec{x}_j(t)} D_{mn}^{\ell*}(\Omega_j(t)) \quad (1)$$

where $\vec{x}_j(t)$ and $\Omega_j(t) = (\psi_j(t), \theta_j(t), \chi_j(t))$ are the centre-of-mass position and orientation (specified by Euler's angles), respectively, of the j th molecule at time t . $D_{mn}^\ell(\Omega)$ are Wigner's rotation matrices. We also introduced the shorthand notation $\kappa \equiv (\ell, m, n)$ where ℓ runs over all positive integers including zero, and m as well as n takes integer values between $-\ell$ and ℓ . Then the molecular two-point correlation functions are given by

$$S_{\kappa\kappa'}(\vec{q}, t) = \frac{1}{N} \langle \rho_\kappa^*(\vec{q}, t) \rho_{\kappa'}(\vec{q}, 0) \rangle. \quad (2)$$

For $\ell = \ell' = 0, 1$ and 2 they are of great experimental importance since they make the main contributions to the light scattering cross section ($\ell = 0$ and $\ell = 2$) and to the dielectric spectra ($\ell = 1$). For neutron scattering all correlators $S_{\kappa\kappa'}$ contribute, but for $|\vec{q}|$ not too large, i.e. $|\vec{q}| \leq q_{\max}$ (the position of the main peak in the centre-of-mass correlator $S_{000,000}(\vec{q}, t)$), correlators with small ℓ and ℓ' make the main contributions [21].

The Mori–Zwanzig projection formalism in conjunction with the mode-coupling approximation provides a closed, coupled set of equations for $S_{\kappa\kappa'}(\vec{q}, t)$ which for its Laplace transform ($S_{\kappa\kappa'}(\vec{q}, z) \equiv \mathbf{S}(\vec{q}, z)$) takes the following form:

$$\mathbf{S}(\vec{q}, z) = - [z\mathbf{S}^{-1}(\vec{q}) + \mathbf{S}^{-1}(\vec{q})\mathbf{K}(\vec{q}, z)\mathbf{S}^{-1}(\vec{q})]^{-1} \quad (3)$$

$$K_{\kappa\kappa'}(\vec{q}, z) = \sum_{\alpha, \alpha' = R, T} \sum_{\mu, \mu' = 1}^3 \sum_{\kappa''\kappa'''} q_{\kappa\kappa''}^{\alpha\mu}(\vec{q}) q_{\kappa'\kappa'''}^{\alpha'\mu'}(\vec{q}) k_{\kappa''\kappa'''}^{\alpha\mu, \alpha'\mu'}(\vec{q}, z) \quad (4)$$

$$\mathbf{k}(\vec{q}, z) = - [z\mathbf{J}^{-1}(\vec{q}) + \mathbf{J}^{-1}(\vec{q})\mathbf{M}(\vec{q}, z)\mathbf{J}^{-1}(\vec{q})]^{-1} \quad (5)$$

where

$$(\mathbf{J}(\vec{q}))_{\kappa\kappa'}^{\alpha\mu, \alpha'\mu'} \equiv J_{\kappa\kappa'}^{\alpha\mu, \alpha'\mu'}(\vec{q}) = \frac{kT}{I_{\alpha\mu}} \delta_{\kappa\kappa'} \delta_{\alpha\alpha'} \delta_{\mu\mu'} \quad (6)$$

is the static current-density-correlation matrix. $q_{\kappa\kappa'}^{\alpha\mu}(\vec{q})$ equals $q^\mu \delta_{\kappa\kappa'}$ for $\alpha = T$ and is related to the angular momentum operators L^μ for $\alpha = R$.

$$I^{\alpha\mu} = \begin{cases} m & \alpha = T \\ I_\mu & \alpha = R \end{cases} \quad (7)$$

is a unified notation for the molecular mass and its principal moments of inertia I_μ . The second term in equation (5) is decomposed into a regular part $\underline{\mathbf{m}}^{reg}(\vec{q}, z)$ accounting for the fast motion and a contribution $\underline{\mathbf{m}}(\vec{q}, z)$ due to slow pairs of density modes. The underbar in \mathbf{k} , \mathbf{J} and \mathbf{m} stands for the additional superscripts $(\alpha\mu, \alpha'\mu')$. Making use of the mode-coupling approximation one finds for the memory kernel $\underline{\mathbf{m}}(\vec{q}, t)$ in the time regime

$$m_{\kappa\kappa'}^{\alpha\mu, \alpha'\mu'}(\vec{q}, t) = \frac{1}{2N} \left(\frac{\rho_0}{8\pi^2} \right)^2 \sum_{\vec{q}_1, \vec{q}_2} \sum_{\substack{\kappa_1, \kappa_2; \\ \kappa'_1, \kappa'_2}} v_{\kappa\kappa_1\kappa_2}^{\alpha\mu}(\vec{q}, \vec{q}_1, \vec{q}_2) v_{\kappa'\kappa'_1\kappa'_2}^{\alpha'\mu'}(\vec{q}, \vec{q}_1, \vec{q}_2) \times S_{\kappa_1\kappa'_1}(\vec{q}, t) S_{\kappa_2\kappa'_2}(\vec{q}, t) \quad (8)$$

where $\rho_0 = N/V$ is the number density and the explicit expression for the factors $v^{\alpha\mu}$ of the vertex functions can be found in reference [19]. It is important to mention that these factors depend on the *static* correlators $S_{\kappa\kappa'}(\vec{q})$, only.

2.2. The glass transition scenario

Similarly to the case for simple liquids, the ideal dynamical glass transition is indicated by nonvanishing nonergodicity parameters:

$$F_{\kappa\kappa'}(\vec{q}) = \lim_{t \rightarrow \infty} S_{\kappa\kappa'}(\vec{q}, t) = - \lim_{z \rightarrow 0} z S_{\kappa\kappa'}(\vec{q}, z). \quad (9)$$

For ℓ and/or $\ell' \neq 0$ they describe the freezing of the orientational degrees of freedom. The question which now arises is: Do translational and orientational modes freeze simultaneously or not? The answer to this question depends on the particle's symmetry.

For instance, for a system of dipolar hard spheres, which is controlled by the packing fraction ϕ and the temperature T , there are two characteristic temperatures T_1 and $T_2 < T_1$ such that only the modes with ℓ and ℓ' even undergo a structural glass transition at a critical line $\phi_c^{(B)}(T)$, and not those with ℓ and ℓ' odd, provided that $T > T_1$. For $T_2 < T < T_1$ the same happens at $\phi_c^{(B)}(T)$. But, on increasing ϕ further, there is a spin-glass-like transition (continuous) at a critical line $\phi_c^{(A)}(T) > \phi_c^{(B)}(T)$ where the modes with ℓ and ℓ' odd freeze, too. At T_2 the critical line $\phi_c^{(A)}(T)$ merges into $\phi_c^{(B)}(T)$ such that all modes freeze simultaneously for $T \leq T_2$. For molecules without any symmetry there exists one temperature T_c (or density n_c) only, where all modes freeze simultaneously [19, 22].

Recently we have speculated that for, e.g., hard ellipsoids it might be possible that the orientational degrees of freedom perform a glass transition into an orientational glass while the centre-of-mass motion remains ergodic [23]. Such a phase would be a *liquid glass*, in analogy to a liquid crystal. Increasing the packing fraction even more should finally result in a freezing of the translational degrees of freedom. These examples demonstrate that the glass transition scenario can be rather rich due to the presence of orientational degrees of freedom and their coupling to the translational motion.

2.3. The two scaling laws

2.3.1. α -relaxation. The α -relaxation describes structural relaxation, which is not influenced by inertia effects. Therefore, on the α -relaxation timescale $\tau(T)$ one may neglect the first term in equation (5). It is easy to prove that the resulting set of equations are invariant under a scale transformation

$$z \rightarrow z/\lambda \quad \lambda \text{ real}$$

or in the time regime under

$$t \rightarrow \lambda t.$$

Consequently, there exist α -master functions $\phi_{\kappa\kappa'}^{(\alpha)}(\vec{q}, x)$ such that

$$S_{\kappa\kappa'}(\vec{q}, t, T) = \phi_{\kappa\kappa'}^{(\alpha)}(\vec{q}, t/\tau(T)). \quad (10)$$

The reader should note that $\phi^{(\alpha)}$ depends on \vec{q} and on κ, κ' . This result is a straightforward generalization of that for simple liquids [2].

2.3.2. β -relaxation. For *simple* liquids it has been proven [2] that there exists a β -relaxation timescale $t_\sigma(T)$ on which the particle is captured in a cage, which leads to

$$S(q, t, T) \equiv F^c(q) + H(q)G(t, T). \quad (11)$$

where $F^c(q)$ is the critical nonergodicity parameter, $H(q)$ the critical amplitude and $G(t, T)$ the so-called β -correlator which is related to the master function $g_\pm(x)$ by

$$G(t, T) = c_\sigma(T)g_\pm(t/t_\sigma(T)). \quad (12)$$

The upper and lower signs refer to $T \leq T_c$ and $T > T_c$, respectively. The correlation scale $c_\sigma(T)$ is proportional to $|T - T_c|^{1/2}$. The proof is based on the positivity of the vertices of the memory kernel which holds for a simple one-component liquid, but not for molecular liquids. This positivity guarantees that the glass transition is driven by only *one* mode which becomes unstable at T_c . However, this condition is sufficient but not necessary. We are convinced that this single-mode instability is the generic case. Therefore equation (11) can be generalized to

$$S_{\kappa\kappa'}(q, t, T) \cong F_{\kappa\kappa'}^c(\vec{q}) + H_{\kappa\kappa'}(\vec{q})G(t, T) \quad (13)$$

where $G(t, T)$ is given by equation (12). The Laplace transform $g_\pm(z)$ fulfils the *same* equation:

$$\mp 1 + \lambda z \text{LT}[g_\pm(t)^2](z) + [z g_\pm(z)]^2 = 0 \quad (14)$$

like for simple liquids [2]. The only influence of the orientational degrees of freedom is in λ (see the comment below). In the vicinity of T_c it is (as for simple liquids)

$$t_\sigma(T) \sim |T - T_c|^{-a/2} T \leq T_c. \quad (15)$$

The condition that the $S_{\kappa\kappa'}$ from (10) and (13) overlap for $t_\sigma \ll t \ll \tau$ fixes $\tau(T)$:

$$\tau(T) \sim (T - T_c)^{-\gamma} \quad T \geq T_c \quad (16)$$

where $\gamma = \frac{1}{2}a + \frac{1}{2}b$ and a and b follow from the exponent parameter λ :

$$\frac{(\Gamma(1-a))^2}{\Gamma(1-2a)} = \lambda = \frac{(\Gamma(1-b))^2}{\Gamma(1-2b)}. \quad (17)$$

$\Gamma(x)$ is the gamma function. λ is the most crucial parameter in the β -regime, and it is related to the static structure factors at T_c . This relationship is not universal and it involves the orientational correlations as well [24].

2.4. Diffusion constants

We restrict our consideration to the rotational diffusion tensor $D_R^{\mu\mu'}$. The equations for D_T , the translational diffusion constant, are similar. Let us first investigate the rotational diffusion tensor $\tilde{D}_R^{\mu\mu'}$ in the body fixed frame which is given by

$$\tilde{D}_R^{\mu\mu'} = \int_0^\infty dt \langle \tilde{\omega}^\mu(t) \tilde{\omega}^{\mu'}(0) \rangle \quad (18)$$

where $\tilde{\omega}^\mu(t)$ is the μ th component of the angular velocity of a tagged particle in its body fixed frame. Using the self-current density

$$\tilde{J}_\kappa^{(s)\alpha\mu}(\vec{q}, t) = i^\ell (2\ell + 1)^{1/2} \tilde{v}^{\alpha\mu}(t) e^{i\vec{q} \cdot \vec{x}(t)} D_{mn}^{\ell*}(\Omega(t)) \quad (19)$$

where

$$\tilde{v}^{\alpha\mu}(t) = \begin{cases} \dot{x}^\mu(t) & \alpha = T \\ \tilde{\omega}^\mu(t) & \alpha = R. \end{cases} \quad (20)$$

We introduce the corresponding self-part of the current-density correlator:

$$\tilde{J}_{\kappa\kappa'}^{(s)\alpha\mu, \alpha'\mu'}(\vec{q}, t) = \left\langle \tilde{J}_\kappa^{(s)\alpha\mu*}(\vec{q}, t) \tilde{J}_{\kappa'}^{(s)\alpha'\mu'}(\vec{q}, 0) \right\rangle \quad (21)$$

It is easy to show that $\tilde{D}_R^{\mu\mu'}$ is determined by the Laplace transform of its rotational part:

$$\tilde{D}_R^{\mu\mu'} = (-i) \lim_{z \rightarrow 0} \lim_{\vec{q} \rightarrow 0} \tilde{J}_{000,000}^{(s)R\mu, R\mu'}(\vec{q}, z). \quad (22)$$

Again using the projection formalism, but now projecting onto $\tilde{j}_k^{(s)\alpha\mu}(\vec{q})$ and $\rho_k^{(s)}(\vec{q})$, the tensorial self-density, we get

$$\tilde{\mathbf{J}}^{(s)}(\vec{q}, z) \simeq -z \left\{ z^2 \mathbf{1} + \tilde{\mathbf{J}}^{(s)}(\vec{q}) [\mathbf{Q}(\vec{q}) + z \mathbf{m}^{(s)}(\vec{q}, z)] \right\}^{-1} \tilde{\mathbf{J}}^{(s)}(\vec{q}) \quad (23)$$

where we neglected the fast part of the memory kernel. $\mathbf{Q}(\vec{q})$ is a bilinear form in $q_{kk'}^{\alpha\mu}(\vec{q})$ which appeared in equation (4). A mode-coupling approximation for $\mathbf{m}^{(s)}(\vec{q}, t)$ can be obtained by projecting the fluctuating force $\tilde{j}_k^{(s)\alpha\mu}(\vec{q})$ onto the bilinear product $\rho_{k'}^{(s)}(\vec{q}')\rho_{k''}^{(s)}(\vec{q}'')$ and subsequent factorization of the four-point correlator. For low enough temperatures the coupling between $\rho_{k'}^{(s)}$ and $\rho_{k''}^{(s)}$ should become so strong that the self-motion freezes. This freezing is accompanied by a $1/z$ pole of $\mathbf{m}^{(s)}(\vec{q}, t)$. Then it follows from (22) that for $z \rightarrow 0$

$$\tilde{\mathbf{J}}^{(s)}(0, z) \rightarrow z \tilde{\mathbf{A}}(0) \quad (24)$$

where the matrix $\tilde{\mathbf{A}}(0)$ does not depend on z . Substituting (23) into (21) results in

$$\tilde{D}_R^{\mu\mu'} = 0 \quad (25)$$

for all temperatures for which the self-motion has undergone an ideal glass transition. One arrives at the same conclusion for the tensor $D_R^{\mu\mu'}$ in the laboratory fixed frame and also for the translational diffusion constant D_T . The latter follows from equation (21) by replacement of R by T (i.e. one has to take the translation part of the self-current-density correlation) and summation over μ .

3. Comparison with MD results

The predictions of the molecular mode-coupling theory were compared with results from a MD simulation for a system of rigid linear molecules [25, 26] and for the SPC/E model for water [19, 27]. Here we will just review the results for the linear molecules. Attention will be particularly drawn to the rotational diffusion tensor.

In figure 1 we show the α -relaxation times $\tau_{\ell m, q}$ of the correlators

$$S_{\ell\ell'}^m(q, t) \equiv S_{\ell m 0, \ell' m 0}(q, t)$$

for $\ell = \ell'$ as a function of temperature. They can be fitted more or less well by the predicted power law (see equation (15)). Although the deviations from a power law become large at the lowest temperatures we can still locate the critical temperature $T_c \simeq 0.475$ (in Lennard-Jones units) within a few per cent. The corresponding γ -values are not identical (as predicted by MCT) but fluctuate by about ten per cent.

The test of the α -scaling law (cf. equation (10)) is presented by figure 2 for e.g. $S_{11}^0(2.8, t)$ and $S_{22}^0(2.8, t)$. Whereas the $\ell = \ell' = 2$ correlator is consistent with equation (10) (and the same is true for the other correlators) it does not hold for the correlator with $\ell = \ell' = 1$,

In the β -relaxation regime we have checked the validity of equation (13). The result is shown in figure 3 for a few correlators. The thick solid line represents the β -correlator $G(t, T)$ (cf. equation (13)). The times for the different correlators were scaled such that the inflection points (see the dot in figure 3) coincided. Whereas the collective density correlator $S_{00}^0(q, t)$ for $q = q_{\max}$, the position of the main peak in the corresponding static correlator, follows $G(t, T)$ over more than four decades in time, this interval has shrunk to about two decades for $S_{00}^0(q, t)$ for $q = q_{\min}$, the first minimum in the static structure factor. This demonstrates that the temperature range over which equation (13) holds depends on the correlator, i.e. on q and (ℓ, ℓ', m) . This is quite consistent with the results of reference [28] which calculates the next-leading order to the asymptotic laws and demonstrates for a system of hard spheres that

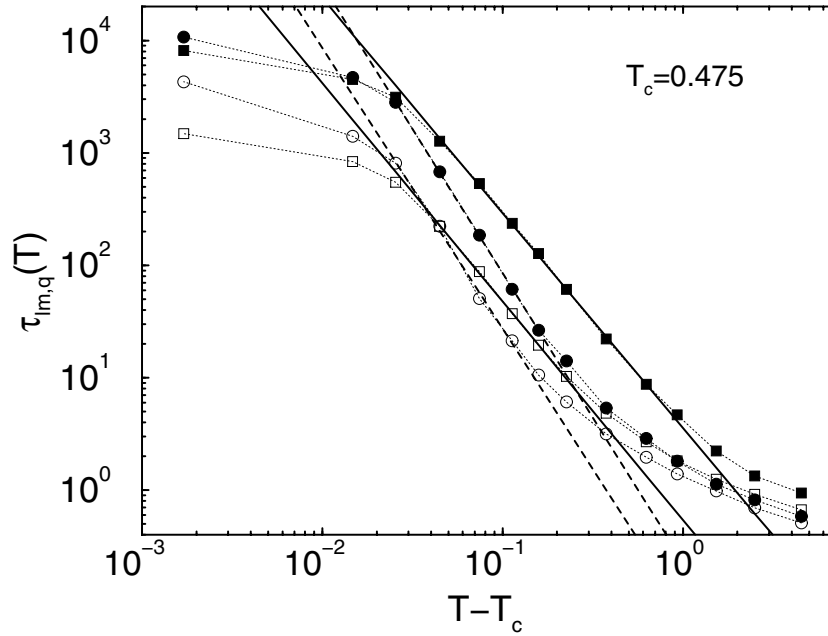


Figure 1. α -relaxation times $\tau_{lm,q}$ versus $T - T_c$ for $m = 0$ and: $q = 2.8, \ell = 1$ (filled squares); $q = 2.8, \ell = 2$ (filled circles); $q = 7.3, \ell = 1$ (open squares); $q = 7.3, \ell = 2$ (open circles). The bold lines represent power laws and the thin lines are a guide for the eye.

the regime where these laws hold depends on the correlator itself. Similarly to the case for α -relaxation, the correlators with $\ell = \ell' = 1$ are not consistent with equation (13).

In figure 4 we depict the temperature dependence of the translational (D) and rotational diffusion constant (D_R) obtained from, respectively, the mean square displacement and from

$$D_R = \sum_{\mu=1}^3 D_R^{\mu\mu} \quad (26)$$

with $D_R^{\mu\mu}$ from equation (17), but $\tilde{\omega}^\mu$ replaced by ω^μ , the angular velocity in the laboratory fixed frame. $D(T)$ becomes rather small when approaching T_c and can be fitted by a power law $(T - T_c)^\gamma$ over about four decades in D . For the highest temperatures, D_R exhibits the same temperature dependence as D , but bifurcates from D at a temperature which is about four times T_c , and then follows an Arrhenius law. This result is in disagreement with what we concluded from the molecular mode-coupling equations.

We have also performed a more stringent test by using the static correlators from the simulation as an input for the MMCT equations in order to calculate the critical nonergodicity parameters $F_{\ell\ell'}^{m,c}(q)$. This was done by truncating the equation at $\ell_{c0} = 2$ [24]. The comparison with the numerical result is shown in figure 5.

Keeping in mind that no fit parameter is used, the agreement is very good for $F_{00}^{0,c}(q)$, but less satisfactory for $F_{22}^{0,c}(q)$. The discrepancy for $\ell = \ell' = 2$ might be related to the truncation at $\ell_{c0} = 2$. Work investigating this point is in progress. The reader should also note that MMCT yields $T_c \approx 0.7521$ [24] which is almost twice the value deduced from the MD simulation. This means that MCT overestimates the ideal glass transition temperature.

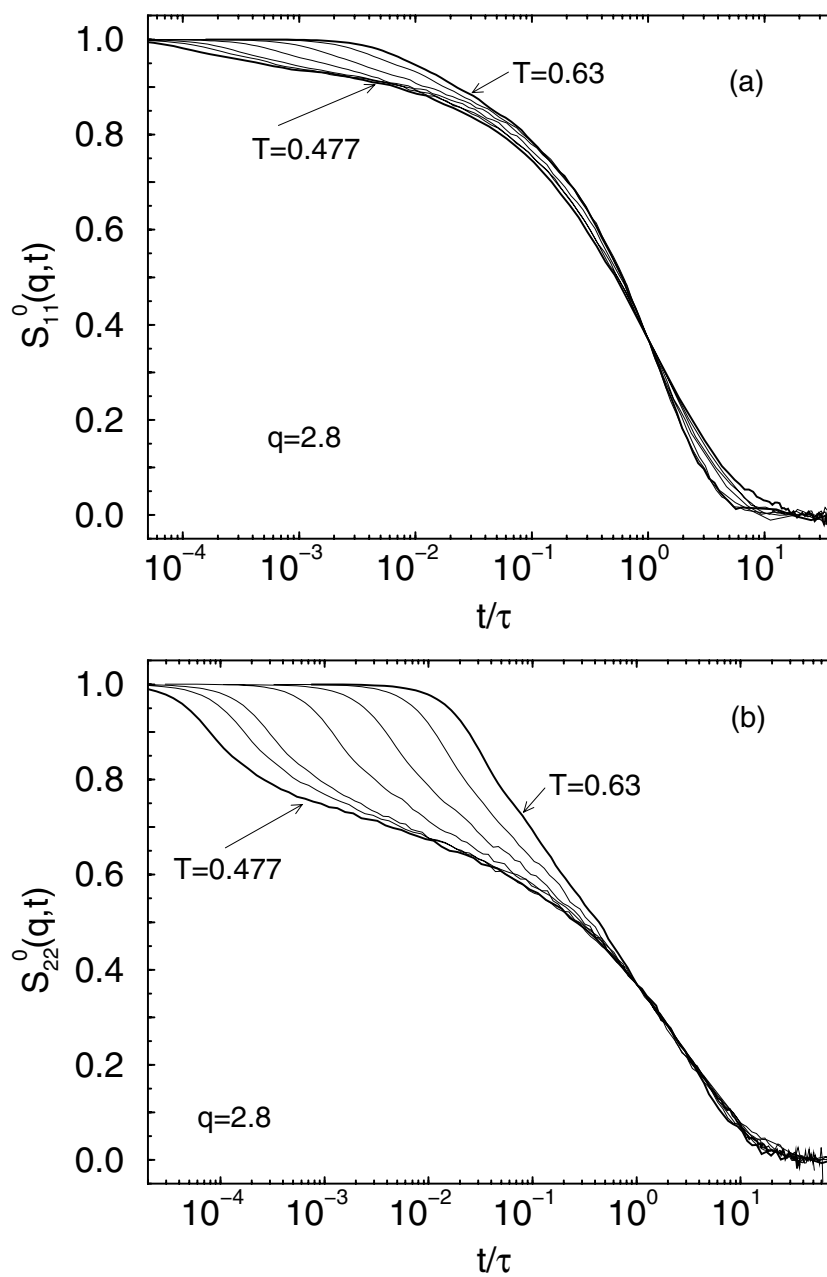


Figure 2. $S_{\ell\ell}^m(q, t, T)$ (normalized by the corresponding static correlator) versus rescaled time $t/\tau(T)$ for $q = 2.8$, $m = 0$ and the seven lowest temperatures of the simulation for (a) $\ell = 1$ and (b) $\ell = 2$.

4. Conclusions

We have demonstrated that many of the features of the supercooled liquid of diatomic molecules can be described well with the molecular mode-coupling equations. The consistency is not

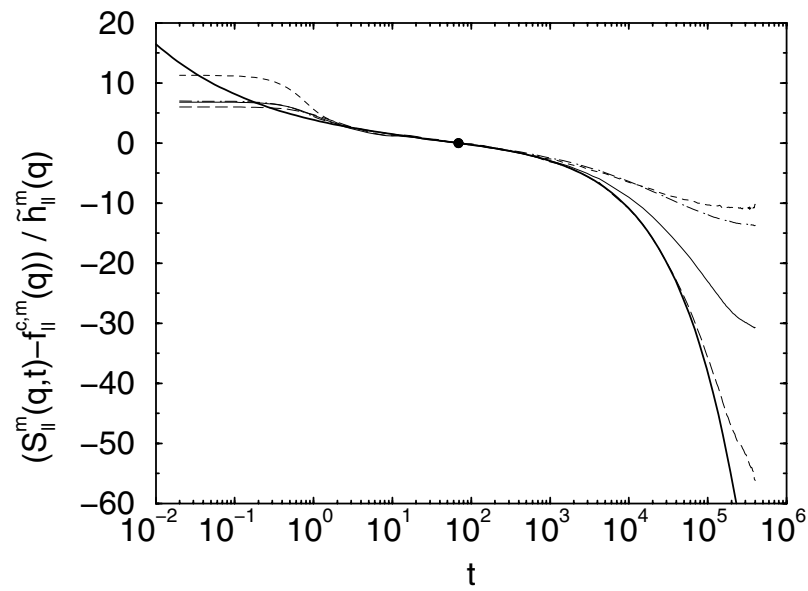


Figure 3. Time dependences of various correlators for $T = 0.477$ shifted by the corresponding nonergodicity parameters and subsequently divided by the critical amplitude: the self-correlator $S_{00}^{(s)0}(q_{max}, t)$ (thin solid line), the collective correlators $S_{00}^0(q, t)$ for $q = q_{max}$ (long-dashed line) and $q = q_{min}$ (short-dashed line) and $S_{22}^{(s)0}(q, t)$ (dashed-dotted line) and the β -correlator $G(t)$ (thick solid line)

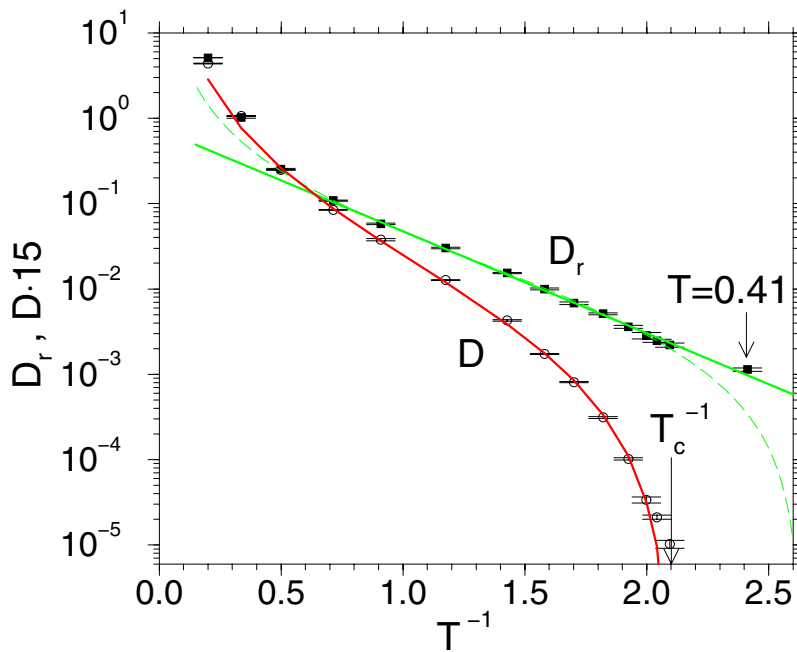


Figure 4. An arrhenius plot for the translational and rotational diffusion constant. D is multiplied by 15 in order to make both curves collapse at high temperatures. The straight line indicates Arrhenius behaviour, the dashed one represents a power law with a critical temperature $T'_c \approx 0.38$ and the dotted line is a guide for the eye.

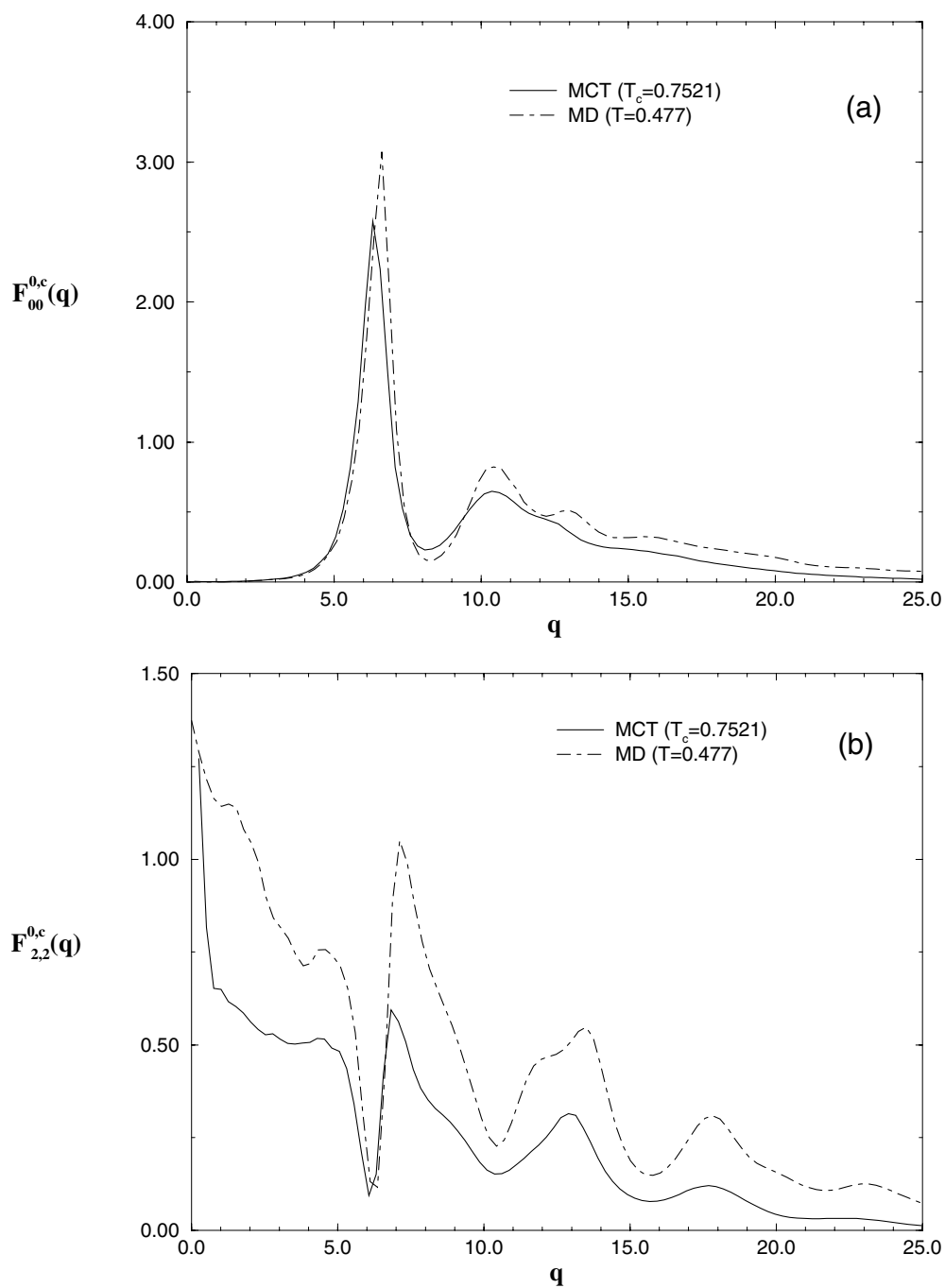


Figure 5. q -dependences of the critical nonergodicity parameters from MMCT (solid line) and simulation (dashed line). (a) $\ell = \ell' = m = 0$ and (b) $\ell = \ell' = 2, m = 0$.

perfect but mostly within the statistical errors. Deviations like those in figure 5(b) are probably due to truncating the equations at $\ell_{c0} = 2$. The main discrepancy occurs for the correlators

with $\ell = 1$ and the rotational diffusion constant.

We have found that the correlators with $\ell = 1$ are strongly influenced by 180° jumps of the molecular axis which are not taken into account by our MCT approach and which correspond to the hopping processes. Another interesting possible explanation has recently been suggested. There it has been shown that for a single dumb-bell molecule within an isotropic liquid in the vicinity of a type-A transition the self-correlators with ℓ even behave qualitatively differently to those with ℓ odd [29]. The failure for the rotational diffusion constant seems to be more serious. Let us assume that a linear molecule with direction $\vec{u}(t)$ is in an ‘orientational’ cage which for simplicity we may choose as a cone along the z -axis and has an angle θ_0 . Then the polar angle $\theta(t)$ of $\vec{u}(t)$ is restricted to between 0 and θ_0 whereas the azimuthal angle $\phi(t)$ of $\vec{u}(t)$ is unrestricted. It is this latter property which allows

$$\left| \int_0^t dt' \vec{\omega}(t') \cdot \vec{e}_z \right|^2 \sim t D_R^{zz} \quad (27)$$

to increase linearly over time. At present it is not obvious how to reconcile this fact (which should also be true for general molecules) with the molecular mode-coupling theory. The orientational cage prevents the relaxation of the self-correlators $S_{\ell m 0, \ell' m' 0}^{(s)}(q, t)$ for ℓ and ℓ' not equal to zero, but it does not lead to a vanishing rotational diffusion constant. This is quite different to the case for the translational degrees of freedom where a perfect ‘translational’ cage makes D zero.

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