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# Modified mode-coupling theory for the collective dynamics of simple liquids

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**Abstract**
Recently it has been shown that mode-coupling theory, which accounts for the salient features
of glassy relaxation near the liquid–glass transition, is also capable of describing the collective
excitations of simple liquids away from the glass transition. In order to further improve the
agreement between theory and computer simulations on Lennard-Jones argon we modify MCT
by taking binary collisions into account. This, in fact, improves the agreement. We also show
that multiplying the memory function of the original theory with a reduction factor leads to
similar results.

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

## 1. Introduction

Understanding the spectral features of the collective excitations in simple liquids as they can be extracted from inelastic neutron (and x-ray) scattering is a long-standing issue [1–6]. A liquid is usually called simple if it is formed by single atoms or molecules and can be described in terms of a pairwise potential. Typical examples are liquid rare gases and liquid metals. For a long time it was not clear whether or not collective, sound-like excitations in simple liquids could be identified by neutron spectra [7–11]. Comparison between experiment and molecular-dynamics simulations [8, 12, 13] became then an important route to gain a deeper insight into the gradual crossover between linear hydrodynamics with well-defined sound excitations and the incoherent high-wavenumber regime. Further insight between the interplay between collective oscillations and relaxational processes can, and has been, achieved by analytical theories. Such an approach is the extension of the kinetic equation concept of dense gases [5, 14]. In the meantime the widely accepted theoretical framework for discussing the collective dynamics of simple liquids is the generalized hydrodynamics approach based on the projector formalism of Mori and Zwanzig [15]. By the projector technique one can represent the Laplace transform of the density–density correlation function (which is the object measured by coherent neutron scattering, see below) in terms of a continued fraction in which the so-called

memory functions (generalized frequency-dependent friction coefficients) play the role of residual terms. The more steps in the continued fraction that are taken into account, the more moment sum rules are taken into account exactly. As many of the properties of the excitation spectrum are determined by the moments, the generalized hydrodynamic approach is superior to approaches in which the validity of the sum rules must be verified for any approximation.

In some early descriptions one took the two-step continued fraction and made an empirical ansatz for the time dependence of the memory function [2]. Attempts to represent the data in terms of a single-exponential memory function gave bad fits. Instead, a fit with a function with two exponentials with different decay constants (relaxation rates) made a much better job both for experimental as well as simulation data [6, 13, 16–19]. Of course, such a procedure is nothing other than curve fitting (albeit an intelligent way) and does not comprise a theory, which must provide explicit expressions for a memory function. Such theories are the different versions of mode-coupling theory. In the older versions [20–25] the three-step formalism has been used. The corresponding memory functions were formulated in terms of products of density–density, density–current and current–current correlation functions. The input of this theory was the interatomic potential and statistical information such as the radial pair distribution function and higher static correlation functions. Although it was possible to describe the measured

and simulated data on liquid rubidium [7, 8] successfully in terms of this theory, it was not easy to obtain an understanding of the interplay between the oscillatory and relaxational motions.

Later a version of mode-coupling theory based on the two-step continued-fraction scheme (from now on called MCT) was established in order to describe the liquid-to-glass transition [26–30]. This theory—it is the *only* available microscopic theory of the glass transition—was highly successful in qualitatively and quantitatively describing the divergence of the viscosity as well as the fractal frequency and time dependence of the glassy relaxation. Quite recently it turned out that MCT is also capable of describing the collective excitations of simple liquids *away from the glass transition*. This holds both for the schematic MCT model [31] and for the full MCT model [32–34] where the only input into the theory is the static structure factor (Fourier transform of the radial pair distribution function). It was shown [32, 33] that the memory functions calculated in MCT for the liquid state just exhibit the two-exponential decay postulated in the evaluations mentioned above. The two time constants describe two different mechanisms: the first one is governed by a microscopic short-time process involving the elastic solid-like collective movements. The second one describes the so-called cage effect, namely the fact that the surrounding particles hinder the diffusive motion of a given particle out of the 'cage' they are forming. The second time constant describes the escape rate from this cage and is extremely density-dependent, whereas the first one is not. This time constant can be identified with the so-called $\alpha$ relaxation time, which is proportional to the viscosity and which diverges within the idealized glass-transition scenario.

A further interesting aspect of the MCT description of collective excitations of simple liquids is the following: the short-time behavior of these excitations shows up in the frequency domain as the characteristic dispersion of sound-like excitations. This dispersion is almost the same in the liquid state as in the glassy state. It is governed by the statistical input, namely the static structure factor. Since the structure factor of simple liquids can essentially be described in terms of that of hard spheres, it was shown and explained in terms of MCT that the excitation spectrum of a number of liquid metals scales with the length scale and compressibility of an effective hard-sphere system used to describe their structure factors [32, 33]. MCT was shown to quantitatively describe the dispersion of these materials without an adjustable parameter. However, a comparison with a computer simulation of Lennard-Jones argon [13] turned out not to be in good agreement with the predictions of MCT [33].

In the present contribution we compare the predictions of MCT with molecular-dynamics simulations of liquid argon as described by a Lennard-Jones potential [12, 13] in more detail. In order to improve the agreement between theory and the data we incorporate binary collision effects as proposed by Sjögren [35, 36] and Götze and Sjögren [37]. We show that the inclusion of these effects improves the agreement. We also show that such an improvement can be achieved as well by multiplying the memory function by a phenomenological

correction factor. Such a correction factor has already been applied by Fabbian *et al* [38, 39] to account for neglecting the rotational degrees of freedom in a liquid composed of non-rotationally symmetric molecules. As the system we investigate here is a simple liquid, such a prefactor may have a different reason, presumably the approximations applied by MCT. As our approach is quite empirical and involves an adjustable parameter, in contrast to the standard version of MCT, the target of this work cannot be an improved version of MCT with more predictive power, but to give some insight, where the deviations between MCT and a computer simulation may come from, and how they may be corrected.

## 2. Formalism

The dynamical structure factor $S(k, \omega)$, which is proportional to the inelastic coherent neutron or inelastic ionic x-ray scattering cross section, is the Fourier transform of the intermediate scattering function $F_k(t)$:

$$S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, F_k(t) e^{-i\omega t}. \qquad (1)$$

This intermediate scattering function $F_k(t)$ can be expressed within the Mori–Zwanzig formalism by a generalized Langevin equation [4, 5, 15]:

$$\ddot{F}_k(t) + \Omega_0^2(k) F_k(t) + \int_0^t dt'\, M_k(t - t') \dot{F}_k(t') = 0 \qquad (2)$$

with the isothermal sound dispersion:

$$\Omega_0^2(k) = v_{\text{th}}^2 k^2 / S(k) \qquad (3)$$

where $v_{\text{th}}$ is the thermal velocity defined by $v_{\text{th}}^2 = k_B T / m$ and a memory function $M_k(t)$. The initial conditions are $F_k(0) = S(k)$ and $\dot{F}_k(0) = 0$.

### 2.1. Original mode-coupling theory

In the original version of MCT [26, 28, 30, 40] $M_k(t)$ is approximated in such a way that it can be represented self-consistently by linear combinations of products of $F_q(t)$ in the following way:

$$M_k(t) = \mathcal{F}_k[F_q(t)] \qquad (4)$$

$$\mathcal{F}_k[F_q(t)] = \frac{n k_B T}{k^2 m} \int \frac{d^3 q}{(2\pi)^3} \frac{1}{2} F_q(t) F_{|\vec{k}-\vec{q}|}(t)$$
$$\times [(\vec{k} \cdot \vec{q}) c(q) + (\vec{k} \cdot (\vec{k} - \vec{q})) c(|\vec{k} - \vec{q}|)]^2 \qquad (5)$$

with the direct correlation function

$$c(k) = \frac{1}{n} \left( 1 - \frac{1}{S(k)} \right) \qquad (6)$$

where $S(k)$ is the static structure factor.

### 2.2. Modified mode-coupling theory

In order to improve the results of MCT we have tried to use a modified version of MCT. This modified version of MCT is based on a theory of Sjögren and Götze [35–37], which

is a generalization of MCT by additionally including binary collisions. The original MCT equations (4) and (5) can be obtained within this theory by neglecting all terms which contain couplings to current correlation functions and binary collision terms. Keeping the binary collision terms leads to the new memory function [35]

$$M_k(t) = M_k^{\mathrm{B}}(t) + \mathcal{F}_k[F_q(t)] - \mathcal{F}_k[F_q^{\mathrm{B}}(t)] \tag{7}$$

with the binary collision term

$$M_k^{\mathrm{B}}(t) = \left( \omega_{\mathrm{E}}^2 + \gamma^l(k) + \frac{k^2 k_{\mathrm{B}} T}{m} n c(k) \right) e^{-t^2/\tau(k)^2} \tag{8}$$

and the Einstein frequency

$$\omega_{\mathrm{E}}^2 = \frac{n}{3m} \int \mathrm{d}^3 r \, g(r) \vec{\nabla}^2 u(r) \tag{9}$$

and

$$\gamma^l(k) = -\frac{n}{m} \int \mathrm{d}^3 r \, e^{-i\vec{k}\vec{r}} g(r) \left( \frac{\vec{k}}{k} \cdot \vec{\nabla} \right)^2 u(r). \tag{10}$$

The third term on the right-hand side of equation (7) has to be subtracted to avoid taking the binary collisions into account twice, because they are already included in $M_k^{\mathrm{B}}(t)$. To further simplify the theory we do not use the function $F_q^{\mathrm{B}}(t)$ suggested by Sjögren et al [35], as it contains the self-part of the intermediate scattering function which would have to be evaluated self-consistently. Instead we use

$$F_k^{\mathrm{B}}(t) = S(k) \exp \left( -\frac{k^2 t^2}{2} \frac{k_{\mathrm{B}} T}{m S(k)} \right) \tag{11}$$

which fulfills the requirement of having the same short-time behavior as $F_k(t)$ and decaying to zero for longer times. The product of the derivative of the pair potential:

$$\nabla_\alpha \nabla_\beta u(r) = \frac{r_\alpha r_\beta}{r^2} u''(r) + \left( \delta_{\alpha\beta} - \frac{r_\alpha r_\beta}{r^2} \right) \frac{u'(r)}{r} \tag{12}$$

with $g(r)$ in equations (9) and (10) can be simplified, because in Lennard-Jones systems $g(r)$ shows a peak, where $u''(r)$ is large and $u'(r)$ small so that [2, 23, 41]

$$g(r) \nabla_\alpha \nabla_\beta u(r) \cong \frac{r_\alpha r_\beta}{r^2} \frac{3}{4\pi} \frac{m}{n r^2} \omega_{\mathrm{E}}^2 \delta(r - r_0) \tag{13}$$
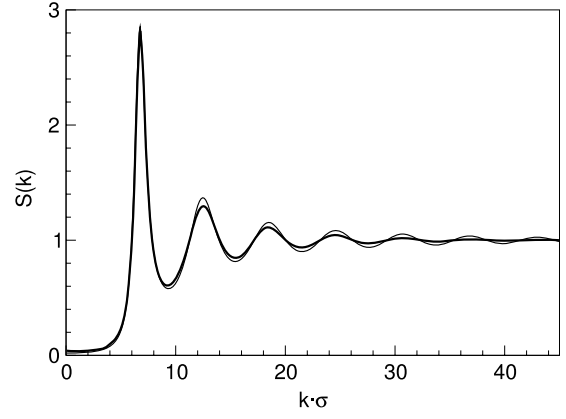
where $r_0 \cong 1.04\sigma$ is the point where $r^2 g(r) u''(r)$ reaches a maximum and

$$\omega_{\mathrm{E}}^2 \cong \frac{4\pi}{3} \frac{n}{m} \int_0^\infty \mathrm{d}r \, r^2 g(r) u''(r) \tag{14}$$

$$\cong 288 \frac{\varepsilon}{m\sigma^2}. \tag{15}$$

Here $\epsilon$ and $\sigma$ are Lennard-Jones units (see section 3). In this approximation equation (10) can be simplified as

$$\gamma^l(k) \cong -3\omega_0^2 \frac{2kr_0 \cos(kr_0) + (k^2 r_0^2 - 2) \sin(kr_0)}{(kr_0)^3}. \tag{16}$$



**Figure 1.** Thick line: static structure factor of a simulation of Lennard-Jones argon by Levesque et al [13]. Thin line: hard-sphere PY static structure factor with $\sigma_{\mathrm{eff}} = 1.026\sigma$ and $\varphi = 0.48$.

The decay time $\tau(k)$ entering the collisional term in equation (8) is assumed to be independent of $k$ and can be used as a fitting parameter. By trying different values for this decay time we obtained a good agreement between our modified MCT calculations and the results of the simulation by using the following expression for the decay time:

$$\tau(k)^{-2} = \frac{u''(r_0)}{m} \cong 0.83\omega_{\mathrm{E}}^2. \tag{17}$$

Another variation of MCT in order to improve the agreement between theory and computer simulation is obtained by using a prefactor $A \neq 1$ in the equation for the memory function:

$$M_k(t) = A \mathcal{F}_k[F_q(t)]. \tag{18}$$

This prefactor can again be used as a fitting parameter. In our calculations (see below) we obtained good agreement with the simulations for $A = 0.65$. This prefactor shifts the glass transition of hard spheres to a critical packing fraction of $\varphi_{\mathrm{c}} = 0.566$ instead of $\varphi_{\mathrm{c}} = 0.516$ [30].
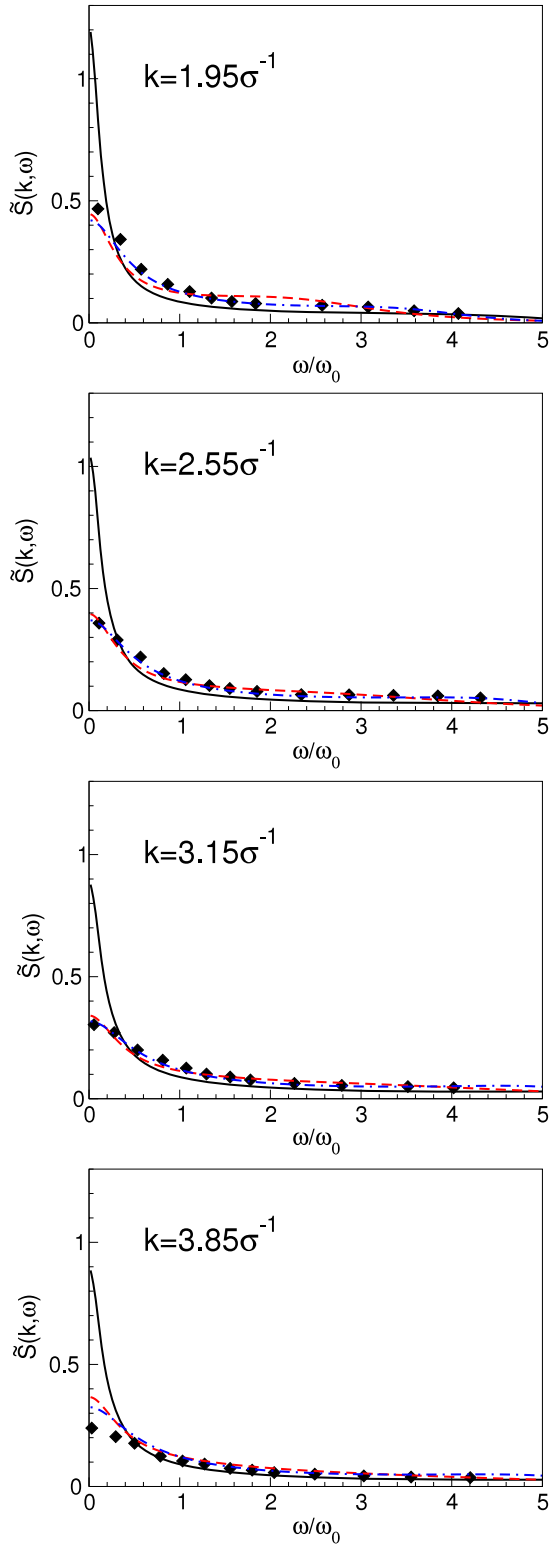
## 3. Comparison with computer simulations on LJ argon

The simulation to which MCT shall be applied to is a simulation of liquid argon [13], which means that the pair potential between two atoms is of a Lennard-Jones type:

$$u(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right). \tag{19}$$
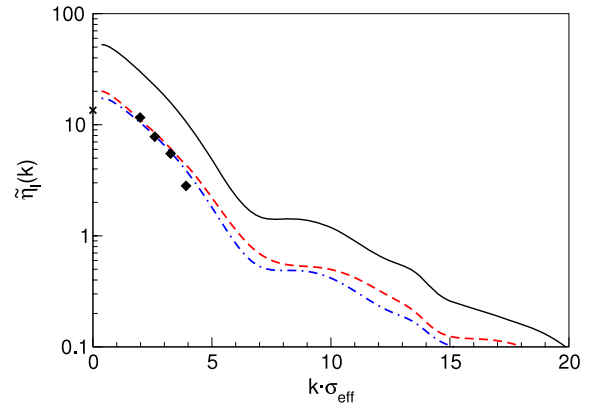
The temperature used for the simulation was $T = 0.723\varepsilon/k_{\mathrm{B}}$ and the density was $n = 0.844\sigma^{-3}$, which corresponds to argon at 86.5 K with a density of 1.418 g cm$^{-3}$. As input for the MCT calculation we used the static structure factor from the simulation by Verlet et al [42] for a system in the same state, where the numerically determined $g(r)$ is extrapolated with the help of the Ornstein–Zernike and the Percus–Yevick relation [5] to larger values of $r$ [42].

This structure factor is compared in figure 1 to the Percus–Yevick structure factor of hard spheres. As can be seen, the

**Figure 3.** MCT result (lines) for the viscosity $\tilde{\eta}_\ell(k)$ as defined in equation (21) compared with the simulation by Levesque *et al* [13] (diamonds). The cross is the value determined experimentally by Naugle *et al* [44]. The same color code is used as in figure 2.



**Figure 2.** MCT result for $\tilde{S}(k,\omega) \equiv S(k,\omega)/S(k) \cdot \omega_0$ (lines) compared with the result of a computer simulation by Levesque *et al* (diamonds) [13]. The solid black line is the result of the standard version of MCT (equation (4)), The red dashed line is the result of the modified theory (equation (7)) and the blue dashed–dotted line is the standard version of MCT with a prefactor (equation (18)) with $A = 0.65$.

simulated structure factor is very similar to that of hard spheres with a packing fraction of $\varphi = 0.48$ and an effective hard-

sphere diameter of $\sigma_{\text{eff}} = 1.026\sigma$. With this static structure factor as input the MCT equations can be solved from which the dynamic structure factor $S(k,\omega)$ can be evaluated. As the length scale we used the effective hard-sphere diameter $\sigma_{\text{eff}}$ and as the frequency scale the isothermal velocity $v_T$ divided by $\sigma$:

$$\omega_0 = \frac{v_T}{\sigma_{\text{eff}}} = \frac{v_{\text{th}}}{\sigma_{\text{eff}}\sqrt{S(k=0)}} = \frac{1}{\sigma_{\text{eff}}}\sqrt{\frac{k_B T}{m S(k=0)}} \quad (20)$$

with $S(k=0) = 1/24.7$ [13]. It should be noted that in these units the isothermal sound velocity is fixed to unity.

In figure 2 we compare the simulational results for the rescaled dynamic structure factor $\tilde{S}(k,\omega) \equiv S(k,\omega)/S(k) \cdot \omega_0$ (solid black line) with the results given by the different versions of MCT. It can be seen that all three versions agree well with the simulations at high frequencies but not at low ones. Here the modified versions give better agreement than the unmodified one.

The quantity $\tilde{S}(k,\omega=0)$ is proportional[3] to the so-called longitudinal $k$-dependent viscosity:

$$\tilde{\eta}_\ell(k) = \frac{1}{\pi n k_B T}\eta_\ell(k) \cdot \omega_0 = S(k,\omega=0)/S(k)^2 \cdot \omega_0$$
$$= \tilde{S}(k,\omega=0)/S(k) \cdot \omega_0. \quad (21)$$

For $k=0$ we have

$$\eta_\ell(k=0) = \eta_v + \frac{4}{3}\eta_s \quad (22)$$

where $\eta_s$ is the usual shear viscosity and $\eta_v$ is the bulk or volume viscosity. Because of this relation between the zero frequency limit of the dynamic structure factor and the generalized viscosity, there is also quite some deviation in the viscosity between the unmodified MCT result and the simulation, as can be seen in figure 3.

The quantitative deviation is related to the fact that MCT underestimates the critical packing fraction at which the glass transition occurs [30]. So the result of the unmodified

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[3] This relation holds only if temperature fluctuations are disregarded, as is done in the present treatment. In the presence of temperature fluctuations $S(k,\omega=0)$ becomes inversely proportional to $k^2\lambda$ at small $k$, where $\lambda$ is the thermal conductivity, see [43].
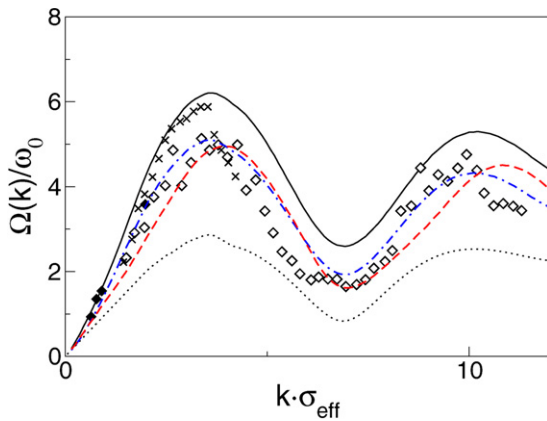
**Figure 4.** Generalized dispersion $\Omega(k)$ calculated from $S(k,\omega)$ via equation (23) for the three versions of MCT, compared with the simulational results of Levesque *et al* [13] (full diamonds) and Rahman [12] (empty diamonds). The crosses are neutron scattering results of de Schepper *et al* [45, 46]. The dotted line is $\Omega_0(k)$ as given in equation (3). The same color code is used as in figure 2.

MCT describes a state which is much closer to the glass transition. This leads to an overestimation of the viscosity. This effect is corrected by the two modified versions of MCT, as demonstrated in figure 3.

In figure 4 we show the generalized sound dispersion defined by

$$\Omega^2(k) = \mathrm{Max}\{\omega^2 S(k,\omega)\} \qquad (23)$$

for the three versions of MCT and compare it with that of the computer simulation. We also included the results of a different computer simulation of Lennard-Jones argon by Rahman [12] in a similar state ($T = 76$ K, $\rho = 1.408$ g cm$^{-3}$) as well as neutron scattering data [45, 46]. As can be seen the agreement for the modified versions is better than for the unmodified one, but the latter already gives quite a good account of the data. It should be noted that the unmodified MCT describes quite well the generalized dispersion of a number of liquid metals, as demonstrated in [32, 33].

## 4. Conclusions

We have demonstrated that mode-coupling theory, which very successful describes the liquid-to-glass transition and the corresponding anomalous relaxation, also gives a satisfactory description of the collective excitations of a simple liquid. The agreement between simulation and analytical theory can be improved either by additionally taking binary collisions into account or by multiplying the memory function with a phenomenological prefactor. This has been demonstrated for the example of liquid argon, described in terms of a Lennard-Jones potential.

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