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Mode-coupling theory of shear and sound relaxation in viscous supercooled liquids

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A generalized mode-coupling theory of shear and ultrasonic relaxation in viscous supercooled molecular liquids is presented. The theory is based on ideas recently proposed to describe dynamical properties of dense simple liquids and then extended by several authors to discuss the glass transition in such systems. The mode-coupling theory naturally involves a continuum of relaxation times leading to a nonexponential decay of the response to mechanical shear and compressional disturbances. The theory provides a good fit of shear and ultrasound data in supercooled molecular liquids over the entire relaxation region.

I. INTRODUCTION

The origin of nonexponential relaxation of mechanical and dielectric disturbances in highly viscous supercooled molecular liquids is a long-standing problem[1] which has recently received renewed interest.[2] The results of experiments in such liquids can often be fitted by assuming that the time dependence of the response function follows the empirical Kohlrausch-Williams-Watts (KWW) form, i.e, $\sim\exp(-t/\tau)^{\beta}$, with τ and β system-dependent parameters.[1–6] The KWW form, as well as other related empirical forms such as those proposed by Barlow, Erginsaw, and Lamb (BEL) and by Cole and Davidson, can be justified by assuming a continuum of microscopic relaxation times with a certain distribution.[1,4] The classical Debye theory, in contrast, predicts an exponential decay of the correlations ($\beta=1$), characterized by a single relaxation time, and fails to describe experiments.

In spite of recent successful attempts to construct models that exhibit a relaxation of the KWW type,[7] there is still not a complete understanding of the microscopic mechanism that leads to the nonexponential behavior in real supercooled liquids.

In this paper a generalized mode-coupling theory is used to describe propagation and absorption of compressional and shear waves in highly viscous liquids over a wide range of frequencies. The generalized mode-coupling theory was recently proposed by Kirkpatrick[8] to explain the discrepancy between the size of the coefficient of the long-time tail ($\sim t^{-3/2}$) of the stress-tensor autocorrelation function predicted by hydrodynamic mode-coupling theory and the value measured for such a coefficient in computer experiments in dense simple liquids. Conventional hydrodynamic mode-coupling theory predicts the $t^{-3/2}$ decay law for long times, but the theoretical coefficient of this long-time tail is approximately 500 times smaller than the observed coefficient. The generalized mode-coupling theory studies the intermediate-length and time-scale contribution to the correlation function[9] by using a mode-coupling formalism where the modes are extended—to large wave numbers—hydrodynamic modes. The theory predicts that at intermediate times the stress-tensor autocorrelation function has a slowly decaying contribution that can be fitted by a $t^{-3/2}$ law, with a coefficient of the correct order of magnitude. At larger times—larger than those considered in computer experiments—this generalized mode-coupling contribution decays exponentially and the usual hydrodynamic long-time tail dominates. At such long times the correlation function has, however, almost decayed to zero. The hydrodynamic long-time tails are therefore not expected to be relevant for any observable behavior of the system. The basic idea of the theory is to recognize that in a dense, highly viscous liquid structural rearrangements on a molecular length scale are very slow, because of the compactness of the microscopic structure. The slowing down of the dynamics of density fluctuations on a molecular length scale affects, in turn, the macroscopic dynamical properties of the fluid via a nonlinear mode-coupling or feedback mechanism. This slowing down of structural relaxation becomes even more dramatic when a liquid is cooled or compressed rapidly below its freezing point and is therefore expected to affect considerably the dynamical properties of supercooled liquids. Furthermore, the self-consistent description of this mode-coupling mechanism was recently used by several authors to discuss the glass transition in simple liquids.[10–13] The self-consistent theory was found to give a solution where the density-density correlation function acquires a nondecaying component. This was identified with the transition to a glassy state with vanishing coefficient of self-diffusion. The work of Leutheusser[10] and of Mazenko[12] differs from the present one because these authors used a simplified model where the wave-vector dependence of the mode-coupling integral was neglected. This approximation is justified when discussing the glass transition in simple liquids,[13] but cannot be used here, as will be discussed below.

The coupling of slowly decaying density fluctuation on molecular length scales is shown here to provide a good description of ultrasound and shear relaxation experiments in molecular supercooled liquids. These are highly viscous liquids—the viscosity can change by several orders of magnitude over a change of temperature of a few decades—exhibiting viscoelastic behavior.

The quantities of interest are the frequency-dependent shear viscosity $\eta_S(\omega)$ and longitudinal viscosity $\eta_L(\omega)$, to be defined below. They are directly related to the shear and longitudinal elastic moduli, $G(\omega)$ and $K(\omega)$, and to the speed of propagation and the coefficient of absorption of a shear or compressional wave in the fluid, respectively.[1] The mode-coupling theory presented here provides a good fit of the frequency dependence of the viscosities over a very wide range of frequencies, covering the transition from a purely viscous response—the imaginary part of the viscosity vanishes with frequency—to a purely elastic response where, for instance, $\eta_S(\omega)\sim G_\infty/(-i\omega)$, with G_∞ the high-frequency shear modulus. The wave-number dependence of the mode-coupling integrals leads to a continuum of microscopic relaxation times and plays an essential role in determining the spread of the relaxation region and the deviation from the classical Debye theory. The theory also predicts the correct order of magnitude of all the quantities of interest.

The fit to experiments is, in general, not as good as that provided by the empirical laws of the KWW type. The main value of the present theory lies in its semimicroscopic character and in the contact it makes with recent predictions for the dynamical properties of dense simple liquids.[8–13] It shows that the same physical mechanism proposed there can account for properties of molecular liquids that can be supercooled in the laboratory.

Finally, it should be mentioned that rather successful phenomenological theories of shear and sound propagation have been developed in the past.[14,15] These theories already contained, even though in a somewhat different context, some of the physical ideas employed here and will be discussed below.

The paper is organized as follows. In Sec. II the mode-coupling theory is outlined and the basic physical approximations are stated. In Sec. III the mode-coupling contributions to the shear and longitudinal viscosities are evaluated by successive approximations. The results are compared with shear and ultrasound experiments in glycerol and hexanetriol. The paper concludes with a brief discussion.

II. MODE-COUPLING THEORY

The basic quantities to be evaluated for a microscopic theory of sound and shear relaxation in liquids are the generalized shear and longitudinal viscosities, defined by

$$\tilde{\eta}_{S,L}(k,z)=\beta\int_0^\infty dt\, e^{zt}\frac{1}{\Omega}\langle \hat{j}_{\mathbf{k}}^{S,L}e^{\hat{L}t}\hat{j}_{-\mathbf{k}}^{S,L}\rangle \;, \tag{2.1}$$

where the thermodynamic limit is intended and $\mathrm{Re}z>0$. The angular brackets denote a grand-canonical ensemble average. Here, $\beta=(k_BT)^{-1}$, with k_B Boltzmann's constant, Ω is the volume of the system, $\hat{j}_{\mathbf{k}}^{S,L}$ a microscopic transverse or longitudinal momentum current at wave vector $\mathbf{k}$, and $\hat{L}$ a microscopic N-particle evolution operator. Their definition is given elsewhere.[16]

The propagation speed and the attenuation coefficient of shear and longitudinal waves are directly related to the frequency-dependent viscosities, defined by[17]

$$\eta_{S,L}(\omega)=\lim_{\epsilon\to0^+}\tilde{\eta}_{S,L}(k=0,z=\epsilon-i\omega)\;. \tag{2.2}$$

If the coupling to temperature fluctuations, which is not expected to affect the frequency dependence of the viscosities, is neglected, the speed of sound $c(\omega)$ and the sound-attenuation coefficient $\alpha(\omega)$ are given by

$$\frac{1}{c(\omega)}+i\frac{\alpha(\omega)}{\omega}=[c_0^2-i\omega\eta_L(\omega)/\rho)]^{-1/2}\;, \tag{2.3a}$$

with $c_0=(\rho\chi_T)^{-1/2}$ the isothermal zero-frequency speed of sound and $\chi_T=(1/\rho)(\partial\rho/\partial p)_T$ the isothermal compressibility. Here $\rho=mn$ is the mass density, with m the molecular mass and n the number density, and p is the pressure. Similarly, the propagation speed $c_S(\omega)$ and the attenuation coefficient $\alpha_S(\omega)$ of a shear wave are related to the shear viscosity $\eta_S(\omega)$ by

$$\frac{1}{c_S(\omega)}+i\frac{\alpha_S(\omega)}{\omega}=[-i\omega\eta_S(\omega)/\rho]^{-1/2}\;. \tag{2.3b}$$

Experimental data are often reported in terms of the finite-frequency elastic shear, bulk, and longitudinal moduli, $G(\omega)$, $K(\omega)$, and $M(\omega)$, respectively. They are related to the viscosities by[1,18]

$$G(\omega)=-i\omega\eta_S(\omega)\;, \tag{2.4a}$$

$$M(\omega)=K(\omega)+\tfrac{4}{3}G(\omega)=K_0-i\omega\eta_L(\omega)\;, \tag{2.4b}$$

with $K_0=1/\chi_T$.

Finally, experimental results are also reported in terms of the complex compliances (the inverse of the moduli), which are defined as the ratio of strain to stress. The definition of the various response functions, as well as a table of the relationship among them can be found, for instance, in Ref. 1.

The objective here is to evaluate the frequency-dependent viscosities by using a generalized mode-coupling theory that takes into account phenomena occurring on a molecular length scale, where the liquid structure is important. It is known that in a dense liquid the decay of density fluctuations on molecular length scales, i.e., length of the order of $2\pi/q_0$, with q_0 the wave vector where the static structure factor has its first maximum, becomes very slow and occurs via self-diffusion.[19–22] This follows from both general considerations and kinetic-theory calculations for a dense hard-sphere fluid.[20,21] Furthermore, evidence for such a slowing down comes from neutron scattering experiments in supercooled liquids of moderate viscosity.[22] The basic assumption of the present work is that also in a supercooled and highly viscous molecular liquid, i.e., liquids with $\eta_S\sim10^6-10^{10}$ P, the slowest structural rearrangements (and consequently those that give the most important contribution to the feedback or mode-coupling mechanism) occur on molecular length scales and take place via self-diffusion. This approximation neglects the contribution from more cooperative structural rearrangements involving groups of molecules. Its validity will be discussed below.

The generalized viscosities depend via mode-coupling effects on the density-density correlation function which, in turn, depends on the longitudinal viscosity. Via this nonlinear feedback mechanism the slowing down of the decay of density fluctuations near q_0 affects the decay of the correlation function that determines the transport coefficients.

On the basis of general considerations, the generalized viscosities can be written as the sum of a bare and a mode-coupling contribution,[16,18]

$$\tilde{\eta}_{S,L}(k,z)=\tilde{\eta}^{B}_{S,L}(k,z)+\tilde{\eta}^{\mathrm{MC}}_{S,L}(k,z)\ . \tag{2.5}$$

The bare contribution can be identified with that predicted by a short-time kinetic equation. For hard spheres, for instance, it can be identified with the value given by the Enskog kinetic equation and it has been computed in detail elsewhere.[20] Its frequency dependence is negligible compared to that of the mode-coupling contribution.

The mode-coupling contributions to the viscosities can be calculated in several standard ways.[16,23] The most important of these contributions is that involving the product of two density fluctuations—it decays the slowest and with the largest amplitude. One then obtains

$$k^2\tilde{\eta}^{\mathrm{MC}}_{S,L}(k,z)=\frac{1}{2\beta}\int'\frac{d\mathbf{q}}{(2\pi)^3}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dz_1}{2\pi i}V_{S,L}(\mathbf{q},\mathbf{k}-\mathbf{q})\times\Phi(\mathbf{q},z_1)\times\Phi(|\mathbf{k}-\mathbf{q}|,z-z_1)\ , \tag{2.6}$$

where $V_{S,L}$ is the mode-coupling vertex or amplitude, to be specified below for the case of interest, and $\Phi(q,z)$ is the normalized dynamic structure factor, given by

$$\Phi(q,z)=\int_0^\infty dt\, e^{-zt}\frac{1}{nS(q)\Omega}\left\langle\sum_{i=1}^{N}e^{-i\mathbf{q}\cdot\mathbf{r}_i}\sum_{j=1}^{N}e^{+i\mathbf{q}\cdot\mathbf{r}_j(t)}\right\rangle\ , \tag{2.7a}$$

with $S(k)$ the static structure factor and $\mathbf{r}_i$ the position of the ith particle. The prime on the q integration in Eq. (2.6) indicates that the integral should be truncated at an upper cutoff q_c of the order of $2\pi/l$ with l the mean free path. In a very dense fluid the mean free path is smaller than the molecular diameter. The extended hydrodynamic description leading to Eq. (2.6) applies then even at lengths of the order of fractions of a molecular diameter. The dependence of the results on this upper cutoff will be discussed below.

Finally, using number- and momentum-conservation laws, $\Phi(q,z)$ can be written in terms of the generalized longitudinal viscosity as[16,18]

$$\Phi(q,z)=\frac{1}{z+q^2/\beta m S(q)[z+q^2\tilde{\eta}_L(q,z)/\rho]}\ . \tag{2.7b}$$

The frequency-dependent viscosities probed in an ultrasound or shear relaxation experiment correspond to the $k=0$ limit of the generalized viscosities of Eq. (2.5). The corresponding mode-coupling contribution is given by

$$\eta^{\mathrm{MC}}_{S,L}(\omega)=\frac{1}{4\pi^2\beta}\lim_{\epsilon\to0^+}\int_0^{q_c}dq\,q^2\times\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dz_1}{2\pi i}\overline{V}_{S,L}(q)\Phi(q,z_1)\times\Phi(q,\epsilon-i\omega-z_1)\ , \tag{2.8a}$$

with

$$\overline{V}_{S,L}(q)=\int\frac{d\hat{\mathbf{q}}}{4\pi}V_{S,L}(\mathbf{q},-\mathbf{q}) \tag{2.8b}$$

or, explicitly,

$$\overline{V}_S(q)=\frac{1}{15}\left[S(q)q\frac{\partial nc(q)}{\partial q}\right]^2 \tag{2.8c}$$

and

$$\overline{V}_L(q)=\tfrac{1}{2}[S(q)]^2\int_{-1}^{1}du\left[q\frac{\partial nc(q)}{\partial q}u^2+n\frac{\partial nc(q)}{\partial n}\bigg|_T-\frac{\gamma-1}{\alpha}\frac{\partial nc(q)}{\partial T}\bigg|_n\right]^2 . \tag{2.8d}$$

Here, $nc(q)=1-1/S(q)$ is the direct correlation function, $\gamma=c_p/c_v$ is the specific-heat ratio, and $\alpha=-\rho^{-1}(\partial\rho/\partial T)_p$ the coefficient of thermal expansion. The last term in parentheses in the integrand in Eq. (2.8c) vanishes for hard spheres.

III. RESULTS AND COMPARISON WITH EXPERIMENTS

In this section the evaluation of the mode-coupling contribution to the frequency-dependent viscosities is outlined and the results are discussed and compared to experiments.

Equations (2.6) and (2.7) constitute a set of self-consistent equations that could, in principle, be solved numerically. This would be in the spirit of the mode-coupling theories of the glass transition.[10–13] Such theories predict, however, a behavior of the zero-frequency shear viscosity η_S as a function of density or temperature that only fits rather moderate viscosity data, i.e., $\eta_S\leq1$–10 P.[11] Here we are interested in liquids with viscosity up to $\eta_S\sim10^8$ P, i.e., in a region where the fully-self-consistent theory would predict the liquid has already formed a glass. The theory presented here differs from the mode-coupling theories of the glass transition in that it is not a truly self-consistent theory. More precisely, instead of evaluating the zero-frequency viscosities self-consistently, their experimental values are used on the right-hand side of Eq. (2.8a). Physically, this approximation is an *ad hoc* way of taking into account the effect of some of the structural relaxation mechanisms that are not included in current mode-coupling theory (such as activated molecular rearrangements).

Before proceeding, one more approximation is introduced to simplify the wave-vector dependence of the right-hand side of Eq. (2.8a). The wave-number dependence of $\Phi(q,z)$ is almost entirely governed by the factor $q^2/\beta mS(q)$ appearing in the denominator of Eq. (2.7b). In dense fluids this factor has a rather deep minimum around q_0 and is responsible for producing the de Gennes narrowing observed in neutron scattering experiments.[20] At such short distances momentum is no longer a conserved quantity and momentum fluctuations relax very quickly via single-particle collisions, with a relaxation rate [proportional to $q^2\tilde{\eta}_L(q,z)/\rho$] that becomes essentially wave-vector independent. For the purpose of evaluating Eq. (2.8), one can then replace $q^2\tilde{\eta}_L(q,z)$ in Eq. (2.7b) by $q_0^2\tilde{\eta}_L(q_0,z)$. The density-density correlation function in Eq. (2.8a) is then approximated by

$$\Phi(q,z)\approx\frac{1}{z+q^2/\beta mS(q)[z+q_0^2\tilde{\eta}_L(q_0,z)/\rho]} . \tag{3.1}$$

In the remainder of this section the right-hand side of Eq. (2.8a) is evaluated by successive approximations.

A. Lowest-order mode-coupling theory

To lowest order the set of Eqs. (2.8a), (3.1), and (2.5) can be closed by neglecting the mode-coupling contribution to the longitudinal viscosity in $\Phi(q,z)$. This is then approximated by a single Lorentzian of the form

$$\Phi^{(1)}(q,z)=\frac{1}{z+q^2/\beta mS(q)q_0^2\nu_L^B(q_0)} , \tag{3.2a}$$

with $\nu_L^B(q_0)=\tilde{\eta}\,_L^B(q_0)/\rho$ the kinematic viscosity. The explicit z dependence of the second term in the denominator of Eq. (3.1) can be shown to be negligible for all the frequencies of interest here and has therefore been neglected. There is both theoretical and experimental evidence, as already mentioned, that the decay of density fluctuations on molecular length scales, i.e., at wave vector near q_0, occurs via self-diffusion. The half-width of the dynamic structure factor in such a q range is $Dq^2/S(q)$, with D the coefficient of self-diffusion.[19–22] One is then led to the identification

$$[\beta mq_0^2\nu_L^B(q_0)]^{-1}\sim D^B , \tag{3.2b}$$

with D^B the bare coefficient of self-diffusion. One then obtains

$$\Phi^{(1)}(q,z)=\frac{1}{z+D^Bq^2/S(q)} . \tag{3.2c}$$

When Eq. (3.2b) is inserted in Eq. (2.8a), the frequency integration can be trivially performed, with the result

$$\eta_{S,L}^{\mathrm{MC}(1)}(\omega)=\frac{1}{4\pi^2\beta}\int_0^{q_c}dq\frac{q^2\overline{V}_{S,L}(q)}{-i\omega+2D^Bq^2/S(q)} . \tag{3.3}$$

Equation (3.3) has been evaluated numerically, using the hard-sphere form for the direct correlation function $c(q)$ (Percus-Yevick approximation[24]), with an effective hard-sphere diameter σ to be considered weakly temperature dependent. For comparison with experiment, the Stokes-Einstein relation between D and η_S is also assumed to hold,

$$D=1/(a\pi\beta\sigma\eta_S) , \tag{3.4}$$

where a is a numerical constant whose value is in the range 2—3. Making use of Eq. (3.4) and letting $x=q\sigma$, Eq. (3.3) becomes

$$\eta_{S,L}^{\mathrm{MC}(1)}(\omega)=\eta_S^B\frac{a}{4\pi}\int_0^{x_c}dx\frac{x^2\overline{V}_{S,L}(x/\sigma)}{-i\omega\tau_D^B+2x^2/S(x/\sigma)} , \tag{3.5}$$

with $x_c=q_c\sigma$ and $\tau_D^B=\sigma^2/D^B$.

As discussed at the beginning of this section, a self-consistent evaluation of $\eta_{S,L}$ using the mode-coupling equation does not lead to the correct order of magnitude for the viscosities for very viscous fluids and would therefore not be appropriate here. Instead, in order to approximately include in the description some of the physical mechanisms governing structural relaxation that are important to determine $\eta_{S,L}$ in the fluids of interest, but are not contained in the self-consistent theories, the bare transport coefficients on the right-hand side of Eqs (3.3) and (3.5) are replaced with their experimental values, denoted by η_S and D.

Since the bare viscosity is always negligible compared to the mode-coupling contribution for the high densities of interest here, from Eqs. (2.4) the elastic moduli are found to be

$$G^{(1)}(\omega)=-i\omega\eta_S^{\mathrm{MC}(1)}(\omega) , \tag{3.6a}$$

$$M^{(1)}(\omega)=K_0-i\omega\eta_L^{\mathrm{MC}(1)}(\omega) . \tag{3.6b}$$

The results can be summarized as follows.

(i) The theory predicts the correct order of magnitude for $\eta_{S,L}=\eta_{S,L}(\omega=0)$. The calculated $G^{(1)}(\omega)$ and $M^{(1)}(\omega)$ fit the results of shear and ultrasound experiments in viscous supercooled liquids such as glycerol in the low-frequency region, i.e., for $\omega\tau_0\leqq 1$, where τ_0 is the longest relaxation time for density fluctuations, i.e., $\tau_0=[Dq_0^2/S(q_0)]^{-1}$. In Fig. 1 the lowest-order theory is

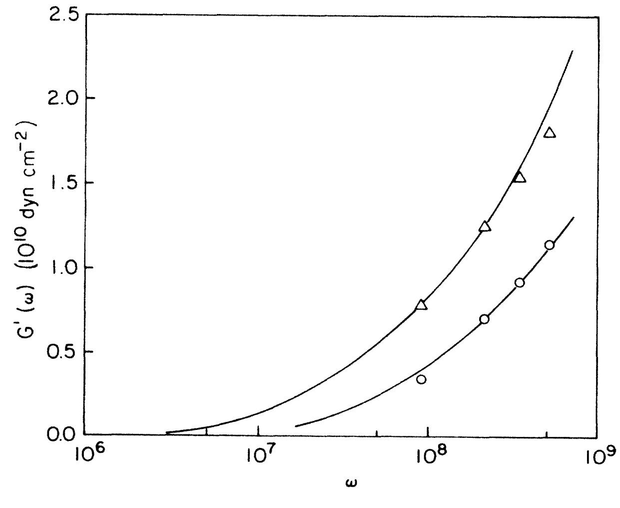

FIG. 1. Re$G(\omega)$ as a function of $\log_{10}(\omega)$, with $\omega=2\pi\nu$, for glycerol at $T=263$ K (△) and $T=275$ K (○), from Ref. 5. The solid curves are the result of the low-order mode-coupling theory. The values of the parameters are given in the text.

compared to data in glycerol from Piccirelli and Litovitz[5] for $T=263$ and 275 K. The quantity plotted is $G'(\omega)=\mathrm{Re}G(\omega)$ as a function of angular frequency $\omega=2\pi\nu$. The theoretical curves are obtained with $\sigma=4.6$ Å (corresponding to $n\sigma^3=0.82$ and 0.81, respectively) and $a=2$. At high frequency the lowest-order theory breaks down—it becomes cutoff dependent, as discussed below, and fails to predict an elastic behavior as $\omega\rightarrow\infty$.

(ii) The value of the zero-frequency viscosities as predicted by Eq. (3.5) is rather cutoff dependent (it can change of a factor of 2). When the zero-frequency value is subtracted out, the frequency-dependent viscosities are essentially independent of the upper cutoff up to $\omega\tau_0\sim 1$. On the other hand, they become very strongly cutoff dependent, even in their functional form, at high frequency. Uncertainty in the numerical value of the viscosities, even at low frequency, also arises from the rather rough approximation used for the static correlation functions in Eq. (3.5) (even for hard spheres the Percus-Yevick approximation overestimates the static correlations near q_0).[24]

(iii) The results of the lowest-order mode-coupling theory for $\eta_{S,L}^{\mathrm{MC}}(\omega)$ are well represented by the following analytical form,

$$\eta_{S,L}^{\mathrm{MC}(1)}(\omega)=\frac{\eta_{S,L}^{\mathrm{MC}(1)}(0)}{1+b_{S,L}-b_{S,L}(1-i\omega\tau_D c_{S,L})^{1/2}}\ , \tag{3.7}$$

where $\tau_D=\sigma^2/D$ and, typically, for $n\sigma^3\sim 0.8-1$, one finds $b_{S,L}\sim 0.25-0.50$. The coefficients c_S and c_L are found to be of the order of $\tau_0/\tau_D=[x_0^2/S(x_0/\sigma)]^{-1}$. It is important to realize that the four constants $b_{S,L}$ and $c_{S,L}$ are not adjustable parameters, but are calculated by the theory. Equation (3.7) is simply a convenient analytical representation of the lowest-order mode-coupling theory at low frequency, i.e., for $\omega\tau_0\leq 1$. If the cutoff is extended to very large q, the functional form of $\eta_{S,L}^{\mathrm{MC}(1)}(\omega)$ becomes cutoff independent over the entire range of frequency and is well represented by Eq. (3.7) everywhere.

B. "Self-consistent" mode-coupling theory

The idea now is to iterate the solution by inserting the result obtained in subsection A for the frequency dependence of η_L^{MC} in Eq. (3.1) and then on the right-hand side of Eq. (2.8a). When doing this it is assumed that the wave-vector and frequency dependence of the generalized viscosities are decoupled and the behavior in frequency obtained for $\eta_L^{\mathrm{MC}}(\omega)=\tilde{\eta}_L^{\mathrm{MC}}(q=0,z=-i\omega)$ is also representative of the frequency dependence of $\tilde{\eta}_L^{\mathrm{MC}}(q_0,z)$. In other words, one approximates

$$\tilde{\eta}_L(q_0,z)\approx\tilde{\eta}_L^{\mathrm{MC}}(q_0,z)\approx\frac{\tilde{\eta}_L^{\mathrm{MC}}(q_0,z=0)}{\tilde{\eta}_L^{\mathrm{MC}}(q=0,z=0)}\tilde{\eta}_L^{\mathrm{MC}}(q=0,z)\ . \tag{3.8}$$

The result of subsection A, i.e., $\tilde{\eta}_L^{\mathrm{MC}(1)}(q=0,z)$, is then substituted into the right-hand side of Eq. (3.5). For convenience, the analytic form of Eq. (3.7) is used in place of the result of the numerical integration of Eq. (3.5). The behavior in frequency of the resulting second approximation for $\eta_{S,L}^{\mathrm{MC}}(\omega)$, denoted by $\eta_{S,L}^{\mathrm{MC}(2)}(\omega)$, no longer depends on the upper cutoff of the wave-vector integration. Elastic response is predicted at high frequency, i.e., $\eta_S^{\mathrm{MC}(2)}(\omega)\sim G_\infty^{(2)}/(-i\omega)$ as $\omega\rightarrow\infty$. The value of the predicted high-frequency shear moduli, $G_\infty^{(2)}$, is still, however, cutoff dependent. To obtain a cutoff-independent result, one more iteration is needed. This is performed by inserting the following form on the right-hand side of Eq. (3.1),

$$\tilde{\eta}_L^{\mathrm{MC}}(q_0,z)\approx\frac{\tilde{\eta}_L^{\mathrm{MC}}(q_0,z=0)}{1+b_L-b_L(1+z\tau_D c_L)^{1/2}+z\tau_D\gamma}\ , \tag{3.9}$$

where γ is a parameter expected to be of the order τ_S/τ_D, with τ_S the Maxwell relaxation time, $\tau_S=\eta_S/G_\infty$.[25] Combining Eqs. (3.9), (3.1), and (2.8a), as well as (3.2b), the corresponding mode-coupling contribution to the viscosities, denoted by $\eta_{S,L}^{\mathrm{MC}}(\omega)$, is given by

$$\eta_{S,L}^{\mathrm{MC}}(\omega)\approx\eta_S\frac{a}{4\pi}\int_0^{x_c}dx\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{d\tilde{z}_1}{2\pi i}\frac{x^2\bar{V}_{S,L}(x/\sigma)}{\tilde{z}_1+x^2/S(x)[1+b_L-b_L(1+\tilde{z}_1c_L)^{1/2}]+\tilde{z}_1\gamma}$$
$$\times\frac{1}{\epsilon-i\omega\tau_D+x^2/S(x)\{1+b_L-b_L[1+(\epsilon-i\omega\tau_D-\tilde{z}_1)c_L]^{1/2}\}+(\epsilon-i\omega\tau_D+\tilde{z}_1)\gamma}\ , \tag{3.10}$$

where $\tilde{z}_1=z\tau_D$ and the limit $\epsilon\rightarrow 0^+$ is intended. Equation (3.10) is again evaluated numerically. The numerical value of $\eta_{S,L}^{\mathrm{MC}}(0)$ and the low-frequency behavior of $\eta_{S,L}^{\mathrm{MC}}(\omega)$ are the same as those predicted by the lowest-order theory described in subsection A. At high frequency Eq. (3.10) leads to elastic behavior, i.e., $\eta_S^{\mathrm{MC}}(\omega)\sim G_\infty/(-i\omega)$ and $\eta_L^{\mathrm{MC}}(\omega)\sim M_\infty/(-i\omega)$, with $M_\infty=K_\infty+\frac{4}{3}G_\infty$, the high-frequency longitudinal modulus. Both the numerical values and the functional form of $\eta_{S,L}^{\mathrm{MC}}$ as a function of frequency are now only weakly dependent on the upper cutoff. In general, the zero-frequency viscosities are more sensitive to the cutoff than the high-frequency moduli. The theory tends to overestimate the former and to underestimate the latter. The numerical values are in general, however, correct up to at most a factor of 2—3.

The predictions of the "self-consistent" theory are compared with experiments in Figs. 2—5. To combine data obtained at different frequencies and temperatures, experimental results and theory are plotted as functions of the reduced frequency $\omega\eta_S/G_\infty$. It is intended here that experimental and theoretical values of the zero-frequency viscosities and of the high-frequency moduli are used to reduce experimental data and theoretical results, respectively.

Figures 2 and 3 display the results of the mode-

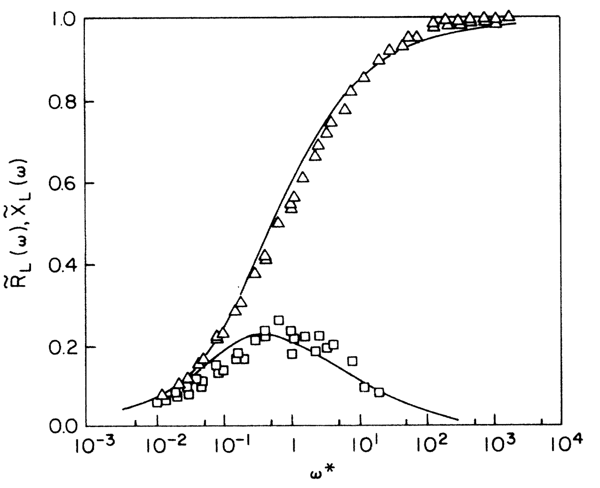

FIG. 2. $\tilde{R}_L(\omega)$ (△) and $\tilde{X}_L(\omega)$ (□) for glycerol (data from Ref. 5) as functions of $\log_{10}(\omega^*)$, with $\omega^* = \omega\eta_S/G_\infty$. The solid curves are the results of the "self-consistent" mode-coupling theory for $a = 3$ and $\sigma = 4.8$ Å.

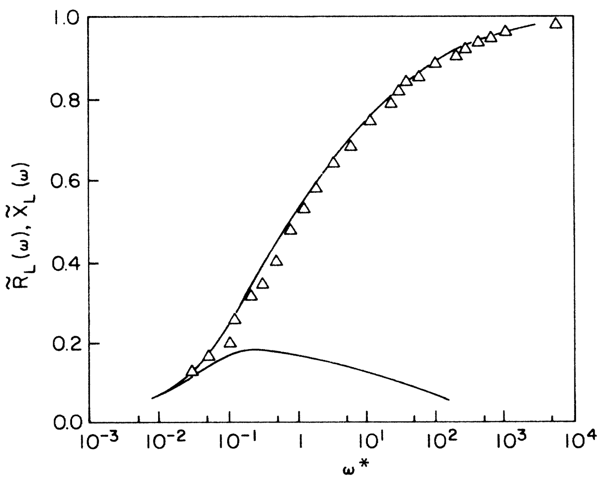

FIG. 4. $\tilde{R}_L(\omega)$ (△) for hexanetriol as a function of $\log_{10}(\omega^*)$ from Ref. 6. The solid curves [$\tilde{X}_L(\omega)$ is also shown] are the present theory for $a = 3$ and $\sigma = 5.5$ Å.

coupling theory for shear and ultrasound relaxation in glycerol, with $a = 3$ and an effective hard-sphere diameter $\sigma = 4.6$ Å. The result of the lowest-order mode-coupling theory is fitted by Eq. (3.7) with $b_L = 0.25$ and $c_L = 0.03$. The data are from Refs. 3 and 5. The functions plotted are the real and imaginary parts of the normalized shear mechanical impedance $\tilde{Z}_L(\omega)$, with

$$\tilde{Z}_L(\omega) = [G(\omega)/G_\infty]^{1/2}$$
$$= \tilde{R}_L(\omega) - i\tilde{X}_L(\omega) , \tag{3.11}$$

and the real and imaginary parts of the normalized longitudinal modulus $\mathcal{M}(\omega)$, given by

$$\mathcal{M}(\omega) = [M(\omega) - K_0]/(M_\infty - K_0)$$
$$= M'(\omega) - iM''(\omega) . \tag{3.12}$$

Finally, in Figs. 4 and 5 the results of the present theory for hexanetriol ($a = 3$ and $\sigma = 5.5$ Å) are displayed. The data are from Ref. 6.

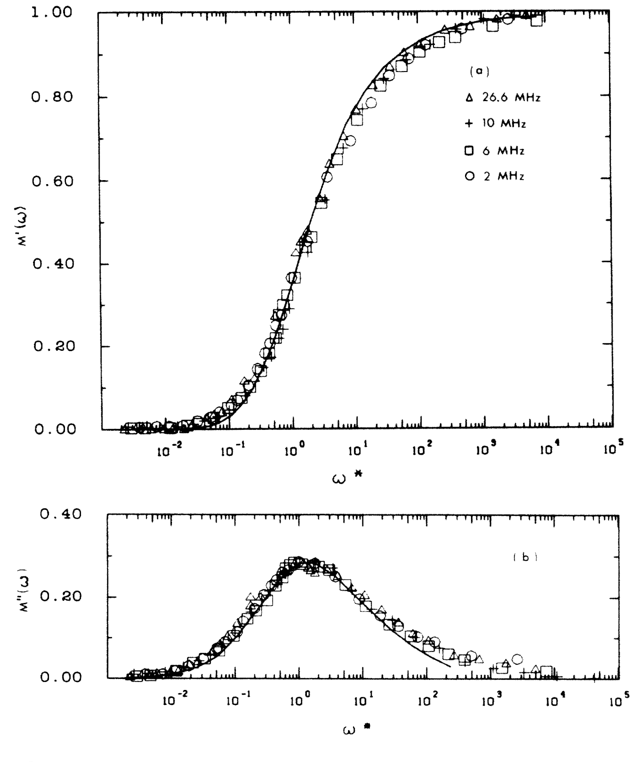

FIG. 3. (a) $M(\omega)$ and (b) $M''(\omega)$ for glycerol. The solid curves are the result of the mode-coupling theory with the same parameters as used in Fig. 2. The data are from Ref. 3, where a similar comparison is also shown.

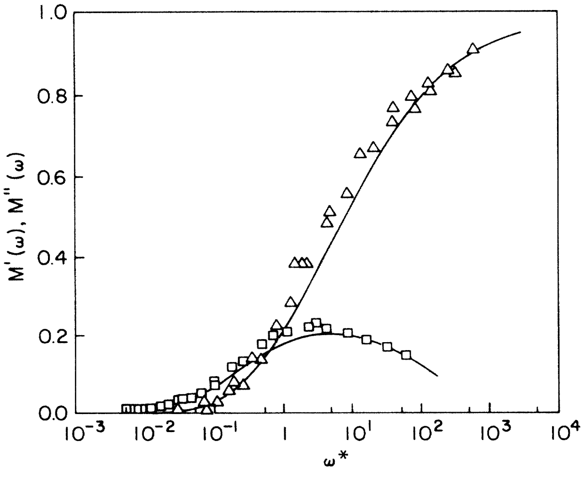

FIG. 5. $M'(\omega)$ (△) and $M''(\omega)$ (□) for hexanetriol (Ref. 6) as functions of $\log_{10}(\omega^*)$. The solid curves are as in Fig. 4.

The predictions of the present theory have also been compared with shear and ultrasound experiments in other supercooled molecular liquids (e.g., butanediol, methylpentanediol). The agreement between theory and experiments is comparable to that obtained for glycerol and hexanetriol.

In contrast with the Debye theory, and in agreement with experiments, the relaxation curves obtained here are in general asymmetric. At low frequency they can be represented as power series in ω^2. At high frequency the absorption curves have a slower tail. The corrections to the high-frequency limit are nonanalytic, e.g., $G(\omega)-G_\infty \approx (-i\omega)^\alpha$, with $\alpha \approx 0.5$ as $\omega \rightarrow \infty$.

IV. DISCUSSION

It has been shown that a generalized mode-coupling theory can be used to describe the propagation of shear and sound waves in viscous supercooled molecular liquids. The theory presented here does not provide a simple analytical form to describe the relaxation of mechanical disturbances in these liquids. It does, however, fit experiments in a variety of supercooled molecular fluids. In this sense it predicts a decay that is equivalent to the empirical KWW form.

The theory is based on ideas recently proposed to discuss dynamical properties of dense simple liquids[8,9] and to predict a glasslike transition in such systems,[10–13] but differs from those in two respects. First, the theory presented here is not a truly self-consistent theory, but uses the experimental values of the static viscosities as an input. Secondly, in some of these dynamical theories of the glass transition the wave-vector dependence of the mode-coupling integrands was neglected. It has been shown that this is a good approximation to obtain the value of the exponent describing the divergence of η_S near the transition.[13] The full wave-vector dependence of the integrals is retained here. This introduces a continuum of relaxation times and is essential in giving the nonexponential relaxation observed in viscous supercooled liquids.

The basic physical assumption behind the present work is that the slowest structural rearrangements in dense liquids occur on molecular length scales via self-diffusion. Their nonlinear coupling determines then the slowing down of the decay of macroscopic correlations. That this is correct even in a supercooled molecular liquid with viscosity as high as 10^8 P may seem questionable. Physically, one might expect that in such liquids structural rearrangements on length scales larger than molecular ones should also be important. A point in favor of the theory presented here, on the other hand, can be drawn by comparing the calculations of $\eta_S^{\mathrm{MC}}(\omega)$ and $\eta_L^{\mathrm{MC}}(\omega)$. The vertex $\overline{V}_S(q)$ is very strongly peaked near q_0 and cuts off almost entirely the contribution from any larger length scales. The vertex $\overline{V}_L(q)$ on the contrary is nonvanishing at $q=0$. In spite of the different behavior of the two vertices, there is experimental evidence[1] that the same physical mechanism is involved in determining both the shear and the longitudinal viscosity. This supports the idea that the contribution from the small-wave-vector region of the integration is not important. Finally, an experiment that would directly test this assumption will be proposed elsewhere.[26]

The theory presented here contains two adjustable parameters: the effective hard-sphere diameter σ and the numerical constant a in the Stokes-Einstein relation [see Eq. (3.4)]. In addition, the mode-coupling vertices have been evaluated by using the hard-sphere form for the static structure factor, $S(k)$. This is a rather crude approximation for the structure factor of a molecular liquid. It appears, however, that the frequency dependence of the viscosities is only weakly sensitive to reasonable variations of the numerical values of the parameters a and σ and to the details of the static structure factor. The numerical values of the mode-coupling contributions to the transport coefficients are more sensitive to the values of the parameters a and σ and—to some extent—to the approximation used for $S(k)$ and to the cutoff of the wave-vector integration, as discussed in Sec. III. It should though be stressed that the possible ranges of values that a and σ can assume are highly constrained. The coefficient a in the Stokes-Einstein relation is approximately known from theoretical estimates in simple fluids [the lowest-order result depends linearly on a—see Eq. (3.4)]. The effective hard-sphere diameter σ is expected to be of the order of a molecular size. It is determined by the requirement that the reduced density $n\sigma^3$ be in the range $n\sigma^3 \approx 0.8$–0.9, with n the actual density of the fluid, so that $S(k)$ is a sensible representation of the structure factor of a dense and highly viscous fluid. Within the range of σ set by the above requirement, the numerical values of the viscosities vary by at most a factor of 2.

Phenomenological theories attempting to relate the idea of a continuum of relaxation times to a model of liquid dynamics have been presented before in the literature.[14,15] The central idea in these theories is that the main contribution to structural relaxation arises from the diffusion of a microscopic ordering parameter describing the deviation of the local liquid structure from its equilibrium value at a given time. To justify this idea the viscous fluid is sometimes[14] described as a microinhomogeneous medium, with liquidlike and solidlike regions. These theories, containing a few free parameters, provide a good fit to experiments. The relevant length scales include length larger than molecular ones. These phenomenological theories rest therefore on the assumption of the existence of rather large solidlike clusters in the fluid.

The idea of diffusion of the local structure is also the central physical mechanism of the present calculation. Here, however, the idea originates from concrete theoretical predictions for hard-sphere fluids[20,21] and from experimental evidence for supercooled liquids of moderate viscosity.[22] The relevant length scale is identified as the molecular length $2\pi/q_0$ and arises naturally from the packed local structure of the fluid. Finally, these physical statements are put here in a more precise and general mathematical framework that makes contact with the dynamical properties of dense fluids in general.

Kirkpatrick and Neiuwoudt[27] have recently reanalyzed the generalized mode-coupling theory of the stress-tensor autocorrelation function of a hard-sphere fluid including dissipative as well as thermodynamic nonlinearities. The effect of dissipative nonlinearities is not included in the Kadanoff-Swift approach used in the earlier theory,[8] nor in the present work, and is usually negligible when calculating long-wavelength effects. They found, however, that dissipative nonlinearities can be as important as thermodynamic ones when considering finite-wave-number effects. By including dissipative nonlinearities, they were able to account for the discrepancy of a factor of 2 between the earlier theory and the computer experiments.

Dissipative nonlinearities could also be important for the effects discussed here. Kirkpatrick and Neiuwoudt give explicit results only for hard-sphere fluids. It is not clear how to apply their theory to more general fluids, since the form of the nonlinear dissipative vertex function is not known in general.

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