

Mode-coupling theory for the shear viscosity in supercooled liquids

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The mode-coupling theory for the shear viscosity for supercooled liquids is generalized so that, in addition to density-fluctuation pairs, current-fluctuation pairs are taken into account. As a consequence the wave-vector and frequency-dependent shear viscosity reproduces in addition to the structural relaxation anomalies the known hydrodynamic long-time tail. In the supercooled state there appears a temperature-sensitive crossover from structural relaxation to the hydrodynamic long-time anomaly. [S1063-651X(98)14005-9]

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I. INTRODUCTION

Since the molecular-dynamics studies of hard disks and hard spheres by Alder and Wainwright and Alder and Alley [1–4] it is well known that some dynamic correlation functions, e.g., the velocity autocorrelation function, exhibit a nonexponential decay for long times of the form $t^{-d/2}$, where d is the dimension of the underlying system. This fractal law does not possess an intrinsic time scale. For long times the dynamics of the systems separates from the microscopic motion and is determined by long-living correlations. Memory effects are important and reflect the cooperativity of the relaxation process on long-time scales. Alder and Wainwright demonstrated that their results can consistently be interpreted within a hydrodynamic model. A numerical solution of the Navier-Stokes equations describes the simulation data after only 20 mean collision times. A backflow pattern is built up which originates from the local displacement of liquid by a moving tagged particle. These long-time tails are also present in the correlation functions that determine the shear viscosity. Ernst *et al.* [5–7] derived the asymptotic time behavior of these correlation functions on the basis of a local equilibrium assumption and the linearized Navier-Stokes equations. The prefactors of the long-time tails are shown to depend only on the transport coefficients of the liquid. In the framework of kinetic theory Dorfman and Cohen could sum up elaborate sequences of collisions of hard spheres and identified the microscopic origin of the long-time tails in leading order of a density expansion [8]. It turns out that the same ring collisions which cause the long-time tails are also responsible for the nonexistence of an analytic expansion of the transport coefficients in powers of the density [9–11].

On the other hand, supercompressed or supercooled liquids exhibit a variety of unusual relaxation processes, often referred to as glassy dynamics. Whereas in gases and normal simple liquids the magnitude of the transport coefficient can be estimated by dimensional considerations, the relevant time scales in glassy liquids depend sensitively on temperature and density. This variation cannot be understood in the framework of activated processes over some energy barrier in the sense of an Arrhenius law. This rapid slowing down of the relaxation manifests itself in the appearance of low-frequency α peaks in the susceptibility spectra [12], which are connected to the structural relaxation of the liquid. A

common feature is the stretching phenomenon. The α -relaxation peak cannot be described by a simple exponential decay; but it can often be fitted reasonably well by a stretched exponential, the Kohlrausch law [12,13]. The microscopic origin of the slowing down is the cage effect, which is a well-known phenomenon in liquid dynamics. The particles rattle in cages formed by their neighbors, before they find the possibility to change their positions over a nearest-neighbor distance. Each particle movement implies therefore a highly cooperative rearranging of the cages.

Leutheusser [14] and Bengtzelius *et al.* [15] proposed a self-consistent mode-coupling theory which identified the feedback of stress and density relaxation via the cage effect as the driving mechanism of a glass transition. Depending on density and temperature one finds ergodic and nonergodic solutions. The theory predicts an ideal glass transition in the sense of Edwards and Anderson [16]. There appears a bifurcation singularity in the dynamics, which separates liquid from glass states. Near the glass-transition singularity leading- and next-to-leading-order asymptotic solutions have been worked out [17]. This work, which is reviewed to a large extent in Refs. [18–20], established some universal features of the bifurcation scenario, such as, e.g., scaling laws.

In this paper we generalize the mode-coupling theory of supercooled liquids of the shear viscosity so that it is possible to describe the cage effect and the long-time tails within the same framework. The theory uses Kawasaki's factorization approximation [21,22] for a transversal force correlation kernel and thereby couples the transversal-stress-tensor correlation function to density- and current-fluctuation pairs. This frequency- and wave-vector-dependent kernel describes the crossover from structural-relaxation dynamics to the hydrodynamic long-time tail. The expression for the kernel resembles the result of a mode-coupling theory for the collective dynamics obtained by Munakata and Igarashi [23]. Their expression, however, does not yield the established prefactor for the long-time tail nor does it give the same cage-effect contribution as formulated in Ref. [15]. We clarify the question of how the long-time tail is suppressed near the glass-transition singularity. A simple scaling analysis explains the sensitive crossover from a singular square-root behavior to regular variation of the reactive part of the long-wavelength shear viscosity.

II. BASIC FORMULAS

The statistical description of a many-particle dynamics is done conventionally in terms of correlation functions. A system of N identical particles of mass m , enclosed in a cube of volume V , shall be considered. The thermodynamic limit with density $n = N/V$ will be anticipated. The particles interact via a rotational invariant pair potential. The implications of translational, rotational, and time-reversal invariance shall be used throughout this paper. From the set of dynamical variables A, B a Hilbert space shall be constructed as usual, exploiting $(A|B) = \beta \langle \delta A^* \delta B \rangle$, $\delta X = X - \langle X \rangle$, $\beta = 1/(k_B T)$ as scalar product. The bracket $\langle \rangle$ denotes canonical averaging. The dynamical variables that we are interested in are the fluctuating density $\varrho_{\vec{q}} = \sum_i e^{i\vec{q} \cdot \vec{r}_i}$ and currents $j_{\vec{q}}^\alpha = \sum_i (p_i^\alpha/m) e^{i\vec{q} \cdot \vec{r}_i}$, where $\alpha = x, y, z$ and \vec{r}_i, \vec{p}_i for $i = 1, \dots, N$ denote particle positions and momenta, respectively. An important quantity is the normalized intermediate scattering function $\Phi_q(t)$, i.e., the correlator for density fluctuations for wave vector \vec{q} : $\Phi_q(t) = (\varrho_{\vec{q}}(t)|\varrho_{\vec{q}})/(\mathcal{N}\beta S_q)$. It depends only on the wave-vector modulus $q = |\vec{q}|$. The prefactor incorporates the static structure factor $S_q = (\varrho_{\vec{q}}|\varrho_{\vec{q}})/(\mathcal{N}\beta)$ and is chosen to enforce the initial condition $\Phi_q(t=0) = 1$.

The normalized current autocorrelation function $\Phi_q^{\alpha\beta}(t) = (j_{\vec{q}}^\alpha(t)|j_{\vec{q}}^\beta)m/\mathcal{N}$ splits into longitudinal and transversal parts

$$\Phi_q^{\alpha\beta}(t) = \hat{q}^\alpha \hat{q}^\beta \Phi_q^L(t) + (\delta^{\alpha\beta} - \hat{q}^\alpha \hat{q}^\beta) \Phi_q^T(t), \quad (1)$$

where $\Phi_q^L(t)$ and $\Phi_q^T(t)$ now only depend on the wave-vector modulus q . Unit vectors are indicated by hats, e.g., $\hat{q}^\alpha = q^\alpha/q$. In this paper we focus on the transversal part Φ_q^T . The density correlation function Φ_q and the longitudinal part Φ_q^L are supposed to be known. They will enter the equations for the transversal correlations. Note that because of the particle number conservation they are related via

$$\partial_t^2 \Phi_q(t) = -\Omega_q^2 \Phi_q^L(t), \quad (2)$$

where $\Omega_q^2 = q^2/(m\beta S_q)$. The characteristic frequency Ω_q defines the time scale of the microscopic motion. In particular, from Eq. (2) one derives the short-time expansion of the density correlation function $\Phi_q(t) = 1 - (\Omega_q t)^2/2 + O(t^4)$. The time evolution is generated by the Hermitian Liouvillian \mathcal{L} , $A(t) = \exp(-i\mathcal{L}t)$; compare Refs. [24–27] for details.

The transversal current correlation function can be expressed in terms of a relaxation kernel within the formalism of Zwanzig and Mori [24–27]. Let us choose \vec{q} parallel to the z direction and introduce the projection operator $\mathcal{P}^T = |j_{\vec{q}}^x\rangle \langle j_{\vec{q}}^x| [m/\mathcal{N}] \langle j_{\vec{q}}^x|$. The perpendicular projector is denoted by $\mathcal{Q}^T = 1 - \mathcal{P}^T$. One derives the exact equation of motion

$$\partial_t \Phi_q^T(t) + \int_0^t M_q^T(t-t') \Phi_q^T(t') dt' = 0, \quad (3a)$$

which relates the transversal current correlators to the correlation functions of the transversal fluctuation forces:

$$M_q^T(t) = (\mathcal{L} j_{\vec{q}}^x | e^{-i\mathcal{Q}^T \mathcal{L} \mathcal{Q}^T t} | \mathcal{L} j_{\vec{q}}^x) \frac{m}{\mathcal{N}}. \quad (3b)$$

Momentum conservation guarantees that $M_q^T(t)$ vanishes proportional to q^2 if $q \rightarrow 0$. The relation to the time- and wave-vector-dependent shear viscosity $\eta_q(t)$ and the corresponding kinematic shear viscosity $\nu_q(t)$ is given by $M_q^T(t) = q^2 \eta_q(t)/(mn) = q^2 \nu_q(t)$.

The relaxation kernel will now be treated within a mode-coupling approximation. As discussed in the Introduction, the relevant fluctuating dynamical variables are chosen to be the density-fluctuation pairs $\varrho_{\vec{k}} \varrho_{\vec{p}}$ and the current-fluctuation pairs $j_{\vec{k}}^\alpha j_{\vec{p}}^\beta$ where $\vec{p} = \vec{q} - \vec{k}$. These are the simplest modes which can cause low-frequency singularities in $M_q^T(t)$. The density pairs are slow because of the tendency to structural arrest [15] and the current pairs are slow because of the momentum conservation law [27]. Because of the symmetry $\vec{k} \leftrightarrow \vec{p}$ one needs only to consider pairs $\vec{k} < \vec{p}$ with some order relation. This convention avoids double counting. Note that these two-particle modes are even with respect to time inversion as is $\mathcal{L} j_{\vec{q}}^x$. The pair modes $\varrho_{\vec{k}} j_{\vec{p}}^\alpha$ have zero overlap with $\mathcal{L} j_{\vec{q}}^x$ because these variables have different time-inversion parity, and therefore the modes $\varrho_{\vec{k}} j_{\vec{p}}^\alpha$ are not considered as relevant. The two-particle-mode matrix elements driven by the reduced Liouville operator $\mathcal{Q}^T \mathcal{L} \mathcal{Q}^T$ are approximated by products of the unprojected single-particle dynamics [22]. Thus the following approximations will enter the calculation of $M_q^T(t)$:

$$\langle \varrho_{\vec{k}}^* \varrho_{\vec{p}}^* \exp(-i\mathcal{Q}^T \mathcal{L} \mathcal{Q}^T t) \varrho_{\vec{k}'} \varrho_{\vec{p}'} \rangle \approx \langle \varrho_{\vec{k}}^*(t) \varrho_{\vec{k}'} \rangle \langle \varrho_{\vec{p}}^*(t) \varrho_{\vec{p}'} \rangle, \quad (4a)$$

$$\begin{aligned} \langle j_{\vec{k}}^{\alpha*} j_{\vec{p}}^{\beta*} \exp(-i\mathcal{Q}^T \mathcal{L} \mathcal{Q}^T t) \varrho_{\vec{k}'} \varrho_{\vec{p}'} \rangle &\approx \langle j_{\vec{k}}^{\alpha*}(t) \varrho_{\vec{k}'} \rangle \\ &\times \langle j_{\vec{p}}^{\beta*}(t) \varrho_{\vec{p}'} \rangle, \end{aligned} \quad (4b)$$

$$\langle j_{\vec{k}}^{\alpha*} j_{\vec{p}}^{\beta*} \exp(-i\mathcal{Q}^T \mathcal{L} \mathcal{Q}^T t) j_{\vec{k}'}^\gamma j_{\vec{p}'}^\delta \rangle \approx \langle j_{\vec{k}}^{\alpha*}(t) j_{\vec{k}'}^\gamma \rangle \langle j_{\vec{p}}^{\beta*}(t) j_{\vec{p}'}^\delta \rangle. \quad (4c)$$

In particular, this implies a factorization of the static four-particle correlations in terms of known two-particle correlations. Restricting oneself to $\vec{k} < \vec{p}$, $\vec{k}' < \vec{p}'$, one obtains

$$\langle \varrho_{\vec{k}}^* \varrho_{\vec{p}}^* \varrho_{\vec{k}'} \varrho_{\vec{p}'} \rangle \approx N^2 \delta_{\vec{k}\vec{k}'} \delta_{\vec{p}\vec{p}'} S_k S_{p'}, \quad (5a)$$

$$\langle j_{\vec{k}}^{\alpha*} j_{\vec{p}}^{\beta*} \varrho_{\vec{k}'} \varrho_{\vec{p}'} \rangle \approx 0, \quad (5b)$$

$$\langle j_{\vec{k}}^{\alpha*} j_{\vec{p}}^{\beta*} j_{\vec{k}'}^\gamma j_{\vec{p}'}^\delta \rangle \approx \frac{N^2}{\beta^2 m^2} \delta_{\vec{k}\vec{k}'} \delta_{\vec{p}\vec{p}'} \delta^{\alpha\gamma} \delta^{\beta\delta}. \quad (5c)$$

Thus one can write the projector $\check{\mathcal{P}}$ onto the subspace spanned by the density and current pairs as the sum of two projectors $\check{\mathcal{P}} = \check{\mathcal{P}}_{\varrho\varrho} + \check{\mathcal{P}}_{jj}$:

$$\check{\mathcal{P}}_{\varrho\varrho} = \sum_{\vec{k} < \vec{p}} |\varrho_{\vec{k}} \varrho_{\vec{p}}\rangle \frac{1}{N^2 \beta S_k S_p} \langle \varrho_{\vec{k}} \varrho_{\vec{p}}|, \quad (6a)$$

$$\check{P}_{jj} = \sum_{\vec{k} < \vec{p}} \sum_{\alpha\beta} |j_{\vec{k}}^{\alpha} j_{\vec{p}}^{\beta}| \frac{m^2 \beta}{N^2} (j_{\vec{k}}^{\alpha} j_{\vec{p}}^{\beta}). \quad (6b)$$

The mode-coupling scheme now consists of sandwiching the reduced time-evolution operator by projection operators $\exp(-i\mathcal{Q}\mathcal{L}\mathcal{Q}t) \rightarrow \check{P} \exp(-i\mathcal{Q}\mathcal{L}\mathcal{Q}t) \check{P}$ and performing the approximations in Eqs. (4). The thermodynamic limit has to be performed by the rule

$$\frac{1}{V} \sum_{\vec{k} < \vec{p}} \cdots \rightarrow \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \cdots. \quad (7)$$

Translational invariance implies $\vec{k} + \vec{p}$ to match the external momentum, say \vec{q} . In order to simplify notation we drop all $\delta_{\vec{q}, \vec{k} + \vec{p}}$ and treat \vec{p} merely as an abbreviation for $\vec{q} - \vec{k}$.

The overlap matrix elements of the transversal force with the density pairs has been discussed before [15,18] and the one with current pairs is also evaluated easily exploiting the identity $(\mathcal{L}A|B) = -i\{A^*, B\}$ where $\{, \}$ denotes the Poisson bracket:

$$\begin{aligned} (\mathcal{L}j_{\vec{q}}^x | \check{\mathcal{Q}}_{\vec{k}} \check{\mathcal{Q}}_{\vec{p}}) &= \frac{n}{m} N S_k S_p (k_x c_k + p_x c_p), \\ (\mathcal{L}j_{\vec{q}}^x | j_{\vec{k}}^{\beta} j_{\vec{p}}^{\gamma}) &= \frac{N}{m^2 \beta} [q^{\beta} \delta^{x\gamma} + q^{\gamma} \delta^{x\beta}]. \end{aligned} \quad (8)$$

Here c_q denotes the direct correlation function connected to S_q by the Ornstein-Zernike relation $S_q = 1/(1 - n c_q)$ [24,25]. The relaxation kernel $M_q^T(t)$ splits naturally into four parts:

$$M_q^T(t) = q^2 \nu_q^{\text{reg}}(t) + M_q^T \text{cage}(t) + M_q^T \text{mixed}(t) + M_q^T \text{ltt}(t). \quad (9)$$

The first term is a regular contribution and reflects the rapidly decaying modes which are not explicitly taken into account by the mode-coupling approximation. If one is concerned only with the long-time dynamics this term can be replaced by a Markovian friction $\nu_q^{\text{reg}}(t) \rightarrow \nu_q^0 \delta(t-0)$.

The second term in Eq. (9) is the coupling to the density pairs and reflects the cage effect, which is a well-known concept in liquid dynamics [26]. It is derived from the expression

$$(\mathcal{L}j_{\vec{q}}^x | \check{P}_{\mathcal{Q}\mathcal{E}} \exp(i\mathcal{Q}^T \mathcal{L} \mathcal{Q}^T t) \check{P}_{\mathcal{Q}\mathcal{E}} | \mathcal{L}j_{\vec{q}}^x) m/N. \quad (10)$$

Applying the approximation, Eq. (4a), and using Eq. (8) one obtains [15,18]

$$\begin{aligned} M_q^T \text{cage}(t) &= \frac{n}{2m\beta} \int \frac{d^3k}{(2\pi)^3} S_k S_p \\ &\quad \times (k_x c_k + p_x c_p)^2 \Phi_k(t) \Phi_p(t). \end{aligned} \quad (11)$$

The term that contains the density-current correlation is derived from the two analogous expressions Eq. (10) with one projector $\check{P}_{\mathcal{Q}\mathcal{E}}$ replaced by \check{P}_{jj} . The continuity equation can be used to express the density-current correlation function in terms of a time derivative of $\Phi_k(t)$:

$$\langle \mathcal{Q}_{\vec{k}}^*(t) j_{\vec{k}}^{\alpha} \rangle = N \beta^{-1} S_k \frac{k^{\alpha}}{k} \partial_t \Phi_k(t). \quad (12)$$

With Eqs. (4b), (8), and (7) one obtains

$$\begin{aligned} M_q^T \text{mixed}(t) &= - \int \frac{d^3k}{(2\pi)^3} \frac{q}{k p} S_k S_p (c_k k_x + c_p p_x) \\ &\quad \times (\hat{k}_z \hat{p}_x + \hat{k}_x \hat{p}_z) \partial_t \Phi_k(t) \partial_t \Phi_p(t). \end{aligned} \quad (13)$$

The last term in Eq. (9) is obtained from the expression of Eq. (10) with both projectors $\check{P}_{\mathcal{Q}\mathcal{E}}$ replaced by \check{P}_{jj} . This term deals with the coupling of the forces to current pairs and will be shown to lead to the long-time tail. The mode-coupling approximation Eq. (4c) and the matrix elements Eq. (8) express this part by current-correlation functions. By Eq. (1) these current-correlation functions can be decomposed into longitudinal and transversal parts. The result reads

$$\begin{aligned} M_q^T \text{ltt}(t) &= \frac{q^2}{2mn\beta} \int \frac{d^3k}{(2\pi)^3} \{ (\hat{k}_z \hat{p}_x + \hat{k}_x \hat{p}_z)^2 \Phi_k^L(t) \Phi_p^L(t) \\ &\quad + [(1 - \hat{k}_z^2)(1 - \hat{p}_z^2) + 2\hat{k}_z \hat{k}_x \hat{p}_x \hat{p}_z \\ &\quad + (1 - \hat{k}_x^2)(1 - \hat{p}_x^2)] \Phi_k^T(t) \Phi_p^T(t) + 2[\hat{k}_z^2(1 - \hat{p}_x^2) \\ &\quad - 2\hat{k}_x \hat{k}_z \hat{p}_x \hat{p}_z + \hat{k}_x^2(1 - \hat{p}_z^2)] \Phi_k^L(t) \Phi_p^T(t) \}. \end{aligned} \quad (14)$$

Note that in the limit $q \rightarrow 0$ all three mode-coupling contributions to the relaxation kernel $M_q^T(t)$ vanish proportional to q^2 ensuring the correct hydrodynamic limit of the liquid state.

Equations (3a), (9), (11), (13), and (14) are the basic formulas of the theory. They represent a closed set of equations for the transversal current correlator. The input quantities consist of the static structure factor S_q , the Markovian friction constant ν_q^0 , and the density-correlation function $\Phi_q(t)$. The longitudinal current-correlation function $\Phi_q^L(t)$ can be evaluated from Eq. (2). Notice that the bare interaction potential does not appear explicitly. The dependence on potential and on external control parameters like temperature and density is hidden in the structure factor S_q or the Ornstein-Zernike direct correlation function c_q , respectively. The mode-coupling approximation thus contains only the renormalized interaction. Because the static structure factor appears to be rather insensitive to details of the microscopic interaction, one expects a certain robustness of the theory.

III. LONG-TIME TAILS

The long-time tails are hidden in the quantity $M_q^T \text{ltt}$. For vanishing external wave vector $q \rightarrow 0$ the integrals over \vec{k} are easily performed. Let us first consider the contribution from the coupling to $\Phi^T \Phi^T$ in Eq. (14), which yields the contribution to the shear viscosity:

$$\nu_0^{TT}(t) = \frac{1}{mn\beta} \int \frac{d^3k}{(2\pi)^3} [1 - \hat{k}_z^2 - \hat{k}_x^2 + 2\hat{k}_z^2 \hat{k}_x^2] [\Phi_k^T(t)]^2. \quad (15)$$

In the hydrodynamic limit, the transversal current correlator deals with a diffusive shear mode

$$\Phi_k^T(t) = \exp(-\nu k^2 t). \quad (16)$$

Here ν denotes the dc kinematic shear viscosity. As usual one shows that this $k \rightarrow 0$ contribution yields the leading long-time asymptote:

$$\nu_0^{TT}(t) = \frac{7}{15mn\beta} \frac{1}{(8\pi\nu t)^{3/2}}, \quad t \rightarrow \infty. \quad (17)$$

The second contribution to the long-time behavior arises from the coupling to $\Phi^L \Phi^L$ in Eq. (14),

$$\nu_0^{LL}(t) = \frac{2}{mn\beta} \int \frac{d^3k}{(2\pi)^3} \hat{k}_z^2 \hat{k}_x^2 [\Phi_k^L(t)]^2. \quad (18)$$

The hydrodynamic limit of the longitudinal current correlator deals with sound waves:

$$\Phi_k^L(t) = \frac{1}{2} e^{-\Gamma_s k^2 t/2} (e^{ickt} + e^{-ickt}). \quad (19)$$

Here c and Γ_s denote the speed of sound and the sound attenuation constant, respectively. For long times, Eq. (18) again approaches a power-law relaxation

$$\nu_0^{LL}(t) = \frac{1}{15mn\beta} \frac{1}{(4\pi\Gamma_s t)^{3/2}}, \quad t \rightarrow \infty. \quad (20)$$

One convinces oneself that there are no further contributions to the leading long-time behavior of the shear viscosity. Equations (17) and (20) reproduce results of the calculations for dilute gases with the assumption of local equilibrium [5–7]. In the low-density limit these are exact results, which have also been derived in the framework of generalized Boltzmann equations [8].

IV. LOW-FREQUENCY SPECTRUM OF THE SHEAR VISCOSITY

A. Further simplifying approximations

In this section we discuss the low-frequency behavior of the shear viscosity in the supercooled state. The density-correlation function has to be evaluated within a separate theory, e.g., the mode-coupling theory of supercooled liquids [19]. Hydrodynamic phenomena of the liquid state can be observed only if the frequencies are smaller than the relaxation rate $1/\tau$ of the α -process contribution to the structural relaxation [18,28]. For frequencies ω exceeding $1/\tau$ the system behaves like a solid, Eqs. (16) and (19) are invalid, and the known long-time anomalies cannot be expected. To study the range of validity of Eqs. (17) and (20) as determined by the structural relaxation we shall consider a generalized hydrodynamical regime. It deals with long-wavelength excitations as does the ordinary hydrodynamics. But it extends the hydrodynamic regime so that all frequencies of order $1/\tau$ are considered. In this regime one can replace with a reasonable accuracy the cage-effect contribution to the generalized viscosity by a stretched exponential or Kohlrausch law $M_q^T \text{cage}(t) \rightarrow \mu e^{-(t/\tau)^{\beta_0}}$. On the time scale τ , the correlators

$\partial_t \Phi_k(t)$ and $\Phi_k^L(t)$ are smaller by a factor $1/\tau$, $1/\tau^2$, respectively, than $\Phi_k(t)$ except for small wave vector k . Small k contributions are important only for the determination of the long-time tails. $M_q^T \text{mixed}(t)$ does not contribute to the latter. The $\Phi^L \Phi^T$ term does not contribute either to the long-time tail in Eq. (14). The $\Phi^L \Phi^L$ contribution yields qualitatively the same long-time contribution to $\nu_0(t)$ as the $\Phi^T \Phi^T$ term. The next simplification consists of ignoring the contribution $M_q^T \text{mixed}(t)$ and all terms in $M_q^T \text{ltt}(t)$ except the $\Phi^T \Phi^T$ coupling. This approximation is certainly not fully justified, because it ignores the long-time tail of Eq. (20), which is responsible for the leading nonanalytic q variation of the shear viscosity [29]. But, for the further discussion these simplifications do not lead to qualitative modifications. The rapid crossover is already understood in terms of the cage effect and the $\Phi^T \Phi^T$ coupling.

The Markovian friction ν_q^0 can be neglected in comparison to the cage-effect contributions. An ultraviolet cutoff Λ has to be introduced in order to make the integral in Eq. (14) convergent. The mode-coupling approximation is not suited to treat short-time dynamics which deal with change of short-distance correlations. It is therefore a standard procedure to eliminate unjustified contributions by short-time cut-offs [26]. However, this procedure does not guarantee the positivity of the spectra, which has to be checked then only afterwards to justify the method. We prefer to eliminate the unphysical terms by a wave-vector cutoff since thereby the analytic properties of the kernel are not altered. The long-time behavior is not affected by either route. Bipolar coordinates for the evaluation of the wave-vector integral are expedient. Let us measure wave numbers in units of Λ and times in units of $[\sqrt{30\pi^2(n\Lambda^{-3})/7}]/(\Lambda v_{\text{th}})$ with $v_{\text{th}} = 1/\sqrt{m\beta}$ denoting the thermal velocity. Correspondingly, the time-dependent kinematic viscosity $\nu_q^{TT}(t)$ is measured in units of $7v_{\text{th}}^2/(30\pi^2 n \Lambda^{-3})$. The resulting set of equations reads

$$\partial_t \Phi_q^T(t) = -q^2 \int_0^t [\nu^{\text{cage}}(t') + \nu_q^{TT}(t')] \Phi_q^T(t-t') dt', \quad (21a)$$

$$\nu^{\text{cage}}(t) = \mu e^{-(t/\tau)^{\beta_0}}, \quad (21b)$$

$$\begin{aligned} \nu_q^{TT}(t) = & \frac{15}{28q} \int_0^1 k \Phi_k^T(t) dk \int_{|q-k|}^{q+k} \frac{k^2 - k_z^2}{2} \left(\frac{1}{p^2} + \frac{1}{k^2} \right. \\ & \left. + \frac{1}{p^2 k^2 q^2} (k^2 - p^2)^2 \right) \Phi_p^T(t) p dp. \end{aligned} \quad (21c)$$

As a first step let us ignore the wave-vector dependence in Eq. (21c). This corresponds to a generalized hydrodynamics model. One obtains a set of equations (21a), (21b), whereas Eq. (21c) has to be replaced by its long-wavelength limit $\nu_0(t) = \nu(t)$:

$$\nu^{TT}(t) = \int_0^1 k^2 \Phi_k^T(t)^2 dk. \quad (21d)$$

The frequency-dependent shear viscosity consists of a reactive part $\nu''_q(\omega)$ and a dissipative part $\nu'_q(\omega)$ defined by

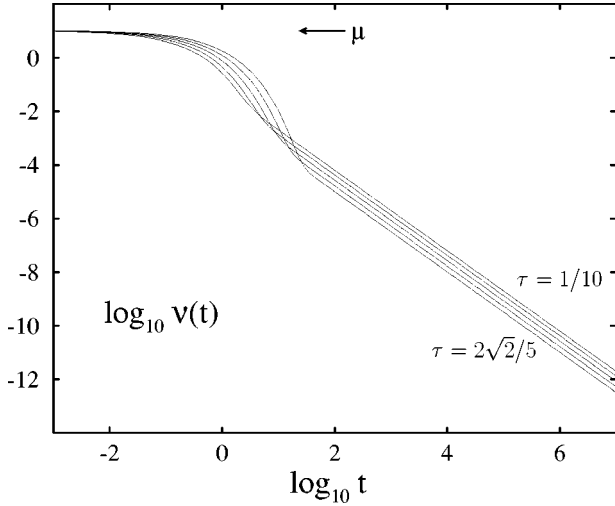


FIG. 1. Time-dependent shear viscosity $\nu(t)$ for the generalized hydrodynamics model, Eqs. (21a), (21b), and (21d), for parameters $\beta_0=0.6$, $\mu=10$ and increasing α -relaxation times $\tau=1/10, \sqrt{2}/10, 1/5, \sqrt{2}/5, 2/5, 2\sqrt{2}/5$. Units are specified in Sec. IV A.

$$\nu'_q(\omega) = \int_0^\infty \nu_q(t) \sin \omega t dt, \quad \nu''_q(\omega) = \int_0^\infty \nu_q(t) \cos \omega t dt. \quad (22)$$

B. Results

Figure 1 exhibits numerical solutions for the viscosity $\nu(t) = \nu^{\text{cage}}(t) + \nu^{TT}(t)$ for the generalized hydrodynamics model on logarithmic scales. The curves are calculated with a discrete set of 100 equally spaced wave-vector moduli. The cooling of the liquid results in a rapid increase of the α -relaxation time τ [12]. Here it is changed on a logarithmic scale; successive curves differ in τ by a factor of $\sqrt{2}$. The Kohlrausch-law long-time tail crosses over within a narrow time window around $t \sim 10$ to the long-time-tail relaxation proportional to $t^{-3/2}$. The range of parameters is chosen such that the short-distance cutoff does not dominate the behavior of the curves. The initial value at $t=0$ is then determined by μ . Not until a decrease of the correlator $\nu(t)$ of four or five decades the long-time tail sets in. The crossover time increases with increasing α -relaxation time. With increasing τ the amplitude of the long-time tail decreases. This results in a crossing of the correlator curves.

The long-time tail leads to a nonanalytic low-frequency behavior. Here we take into account only the long-time tail due to a pair of diffusive shear modes, Eq. (17). The low-frequency spectrum is then given by

$$\nu'(\omega \rightarrow 0) = \nu - \frac{7}{240mn\pi\beta\nu^{3/2}} \sqrt{\omega}, \quad (23)$$

$$\nu''(\omega \rightarrow 0) = \frac{7}{240mn\pi\beta\nu^{3/2}} \sqrt{\omega}, \quad (24)$$

where $\nu = \nu'(\omega=0) \sim \tau$ denotes the kinematic viscosity. The frequency-dependent shear viscosity for our model is exhibited in Fig. 2. One observes an almost constant dissipative part $\nu'(\omega)$, i.e., a white noise spectrum, up to frequencies $\omega \sim \tau^{-1}$. The square-root anomaly, Eq. (23), is not visible on

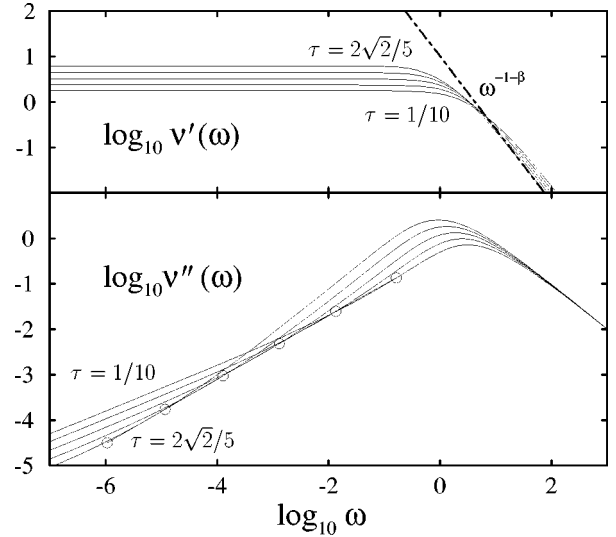


FIG. 2. Real part $\nu'(\omega)$ and imaginary part $\nu''(\omega)$ of the dynamical shear, Eq. (22), as a function of frequency ω for the results shown in Fig. 1. The dashed-dotted straight line indicates the von Schweidler asymptote, Eq. (25), for $\tau=2\sqrt{2}/5$. The circles mark the crossover points $(\omega_{co}, \nu''_{co})$.

this scale. In supercooled liquids τ is very large and therefore the first contribution in Eq. (23) dominates the second one. For frequencies $\omega \gg \tau^{-1}$ one identifies the von Schweidler-law asymptote of the α process:

$$\nu'(\omega \gg 1/\tau) = \mu \sin(\pi\beta/2) \tau^{-\beta} \omega^{-\beta-1} \Gamma(1+\beta), \quad (25)$$

$$\nu''(\omega \gg 1/\tau) = \mu/\omega - \mu \cos(\pi\beta/2) \tau^{-\beta} \omega^{-\beta-1} \Gamma(1+\beta). \quad (26)$$

The reactive part of the shear viscosity $\nu''(\omega)$, in contrast, exhibits the low-frequency nonanalytic contributions; there appears a flattening towards the square-root anomaly. The crossover frequency near ω_{co} that separates the nonanalytic from the regular part of $\nu''(\omega)$ sensitively depends on the time scale τ . The high-frequency part of $\nu''(\omega)$ is in leading order independent of τ , the curves fall on top of each other for frequencies $\omega \gg \tau^{-1}$.

Figure 3 exhibits the variation of the dc shear viscosity $\nu = \nu'(\omega=0)$, the peak height $\nu''_{\text{max}} = \nu''(\omega_{\text{max}})$, and the peak position ω_{max} of the reactive part of the shear viscosity as a function of the α -correlation time τ .

Different strategies are possible to define a crossover frequency for the onset of the long-time anomaly. We divided $\nu''(\omega)$ by $\omega^{3/4}$. Then the $\omega^{1/2}$ part transforms into a decreasing $\omega^{-1/4}$ law whereas the regular contribution $\propto \omega$ translates to an increasing $\omega^{1/4}$ wing. Between these two asymptotes there is a shallow minimum. We define this minimum frequency as the crossover frequency ω_{co} of $\nu''(\omega)$ and the corresponding viscosity value as $\nu''_{co} = \nu''(\omega_{co})$. The crossover points are included in Fig. 2 as circles. Figure 4 exhibits the crossover frequency ω_{co} and the crossover viscosity ν''_{co} as a function of the α -time scale τ . Even though τ is changed only by a factor of $4\sqrt{2}$, the crossover frequency shifts by more than five orders of magnitude. Similarly, the crossover viscosity drops by almost four decades.

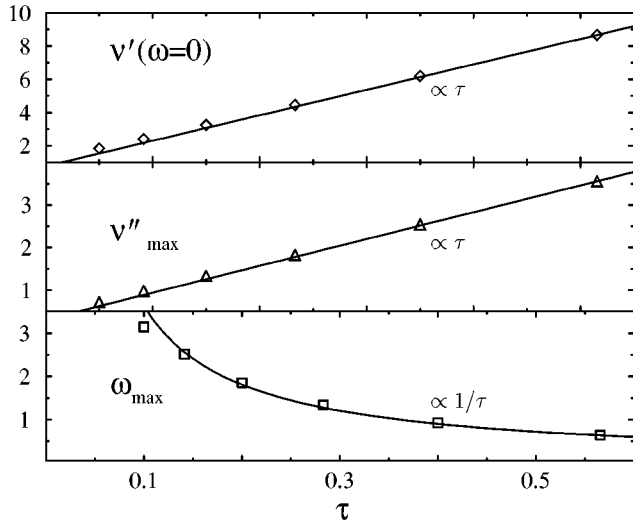


FIG. 3. The dc shear viscosity $\nu'(\omega=0)$ (diamonds), the maximum height $\nu''_{\max} = \nu''(\omega_{\max})$ (triangles), and the corresponding peak position frequency ω_{\max} (squares) as a function of the α -time scale τ for the results shown in Fig. 2. The full lines are the asymptotic laws; the prefactors are chosen such that the curves match the last point.

While the zero-wave-vector shear viscosity exhibits the long-time tail proportional to $t^{-3/2}$, the nonzero-wave-vector shear correlation function relaxes exponentially. However, there appears a finite time window where the shear correlation function $\nu_q(t)$ is almost indistinguishable from its long-wavelength counterpart. Figure 5 exhibits numerical solutions of Eqs. (21a), (21b), and (21c) using a discrete set of 200 wave vectors. For times shorter or comparable to the α -time scale τ the curves fall on top of each other. However, for times larger compared to τ the curves fan out. The relaxation crosses over from a power law to exponential relaxation. A rough explanation is given by the following argument. The vertex in Eq. (14) is regular in the limit $q \rightarrow 0$. However, the transversal current correlators depend expo-

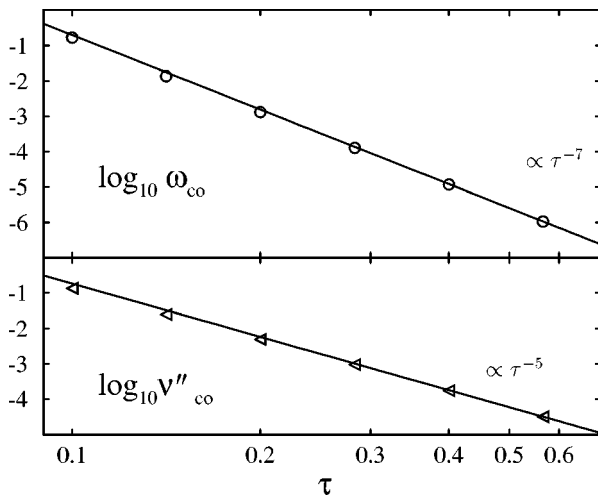


FIG. 4. Double logarithmic representation of the crossover frequency ω_{co} (circles) and the corresponding value $\nu''(\omega_{co}) = \nu''_{co}$ (triangles) as a function of the α -time scale τ for the shear correlation exhibited in Fig. 1. The straight lines indicate the asymptotic laws, Eqs. (29) and (30).

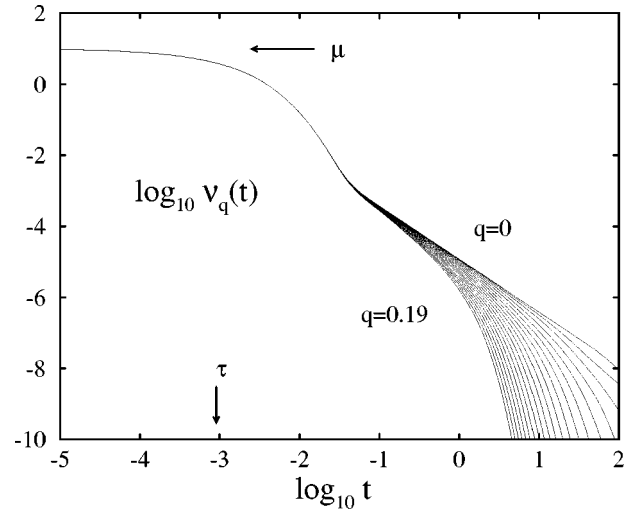


FIG. 5. Time- and wave-vector-dependent shear viscosity $\nu_q(t)$ within the model Eqs. (21a), (21b), and (21c) for parameters $\beta_0 = 0.6$, $\mu = 10$ and $\tau = 0.0009$. Subsequent curves differ in wave-vector modulus q by 0.01.

entially on the wave number. If one assumes for both correlators its hydrodynamic limit one obtains

$$\begin{aligned} \Phi_k^T(t)\Phi_p^T(t) &\approx \exp(-2\nu k^2 t + 2\nu \vec{q} \cdot \vec{k} t - \nu q^2 t) \\ &= \exp[-2\nu(\vec{k} - \vec{q}/2)^2 t] \exp(-\nu q^2 t/2). \end{aligned} \quad (27)$$

After integrating over all wave numbers \vec{k} there remains as dominating factor the exponentially fast relaxing term $\exp(-\nu q^2 t/2)$. This observation fits in the picture of the long-time tail as a consequence of two interfering diffusive shear modes. A small mismatch q of the two shear modes results in a perturbation of the flow profile on large length scales. Not until the remaining correlation arises from a small region in wave-number space that is comparable in its size with the mismatch q does an exponential decay evolve. In particular, the theory predicts a prefactor for this intermediate long-time tail that is independent of q . Merely the extent of the range where the shear correlation function exhibits an intermediate long-time tail is sensitively dependent on the external wave number q . We do not expect the details of the q variation to be correct because the sound modes are known to lead also to a nonanalytic dispersion relation for the shear viscosity with respect to q [29].

Figure 6 exhibits the frequency-dependent shear viscosity for different wave numbers. The real part $\nu'_q(\omega)$ is dominated by the Fourier transform of the Kohlrausch function. The reactive part, however, exhibits on its low-frequency wing a wave-number-sensitive feature. For $q=0$ one finds a bending from the low-frequency anomaly to regular relaxation at the crossover frequency ω_{co} . For nonzero q there appears a second crossover. For very low frequencies one infers a range of regular relaxation, which reflects the exponential decay of the shear correlation function in the time domain. At higher frequencies a range follows that reflects the long-time tail and accordingly exhibits a $\omega^{1/2}$ law. In between one identifies a knee. At even higher frequencies

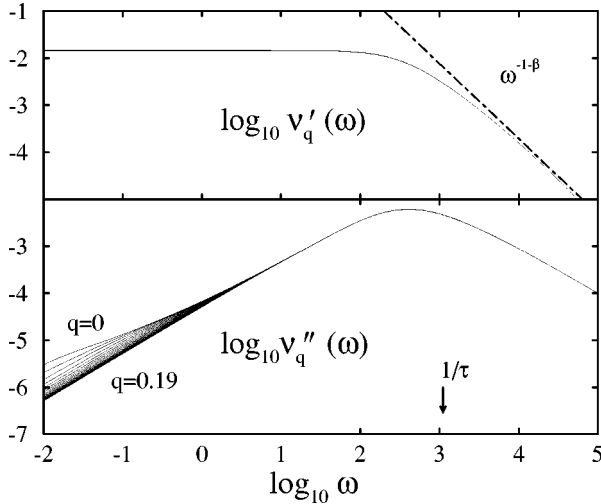


FIG. 6. Real part $v'_q(\omega)$ and imaginary part $v''_q(\omega)$ of the dynamical shear for the results shown in Fig. 5. The dashed-dotted straight line indicates the von Schweidler asymptote, Eq. (25).

but below the α -peak position one observes again a range of regular relaxation. In Fig. 6 this range extends up to the peak maximum. The reactive part of the shear viscosity is characterized by a sequence of different power laws separated by two crossover frequencies. For large wave number q the two crossover frequencies merge and one finds only regular relaxation on the low-frequency wing of the α peak. Let us remark that a fine tuning of the parameter τ was necessary in order to observe all these mentioned features within the numerically accessible time and frequency window. For sufficiently small wave number the correlators are close to its long-wavelength counterpart for times smaller than a q -dependent crossover time or frequencies larger than a q -sensitive crossover frequency. The qualitative features are thus not affected by the appearance of additional q -sensitive crossover phenomena.

Let us add some general qualitative considerations. The α -time scale increases rapidly by lowering the temperature and so does the dc shear viscosity. This in turn implies a suppression of the amplitude in the long-time tail, Eq. (17). Thus glassy relaxation suppresses more and more the long-time anomaly and the crossover becomes visible only below some crossover frequency ω_{co} . The α peak in the dissipative part remains nearly unchanged and, according to Eqs. (23) and (24), the shear viscosity scales as $v'(\omega \rightarrow 0) \sim \tau$, $v''(\omega \rightarrow 0) \sim \tau^{-3/2} \omega^{1/2}$. Above this crossover frequency one finds a regular linear spectrum for $v'(\omega)$. The maximum value is located at $\omega \sim 1/\tau$ and is of the order τ ,

$$v''(\omega_{co} \ll \omega \ll 1/\tau) \sim \tau(\omega\tau). \quad (28)$$

The asymptotic dependence of the dc shear viscosity $v'(\omega = 0)$, the peak height in the reactive part v''_{max} , and the maximum position ω_{max} on τ are indicated in Fig. 3 by solid lines. The scaling behavior of the crossover frequency ω_{co} is now determined by matching the two asymptotic descriptions, Eqs. (24) and (28): $\tau^{-3/2} \omega_{co}^{1/2} \sim \tau^2 \omega_{co}$. Thus the crossover frequency scales as

$$\omega_{co} \sim \frac{1}{\tau^7}. \quad (29)$$

The height of the crossover point is also easily calculated. Evaluating Eq. (28) for the crossover frequency Eq. (29) one obtains

$$v''_{co} \sim \frac{1}{\tau^5}. \quad (30)$$

The prediction of Eqs. (29) and (30) are indicated in Fig. 4 by straight solid lines. Note that in the derivation of the rapid variation for the crossover point in the reactive part of the shear viscosity no assumption for the shape of the α peak was needed. The results therefore do not rely on the Kohlrausch law but hold equally well for other shapes of the primary relaxation peak. The shape of the α -relaxation process merely determines the factors of order unity left out in Eqs. (29) and (30).

V. CONCLUSION

In this paper we presented a theory for the wave-number- and frequency-dependent shear viscosity in the framework of the mode-coupling theory. The derived equations naturally generalize the mode-coupling theory of supercooled liquids [15,18]. The coupling to current pairs permits us to describe the hydrodynamic long-time tails of the shear viscosity and the slowing down due to structural relaxation within a unified theory. The approximations result in a memory kernel that splits naturally into four parts. The first one describes the coupling to all fast decaying relaxation channels and results in some regular contribution to the shear viscosity. The second one contains the coupling to density fluctuations and is responsible for the cage effect; it yields the rapid increase of the dc shear viscosity due to the slowing down of the structural relaxation. The third one includes time derivatives of the density fluctuations and reflects the coupling of density and longitudinal currents. Finally, the fourth one contains products of current correlation functions. The physical picture behind these terms is the backflow which also provides a demonstrative explanation of the long-time tails. The vertices of the theory are explicitly wave-vector dependent and incorporate the interaction potential only indirectly via the static structure factor. The long-time behavior of the different contributions to the shear viscosity is calculated analytically. The prefactors of the long-time tail due to two diffusive shear modes and two interfering sound modes match those of earlier calculations. The equations have to be regularized at high wave numbers. The breakdown of mode-coupling theories at short distances is not a new phenomenon. However, the low-frequency behavior of the shear viscosity is not sensitive to changes in the cutoff, provided the cutoff is not chosen too large.

Within a generalized hydrodynamic approximation of the theory the low-frequency behavior of the shear viscosity is calculated. The dominant contribution arises from the coupling to density modes. All other contributions are small, but contain the long-time tails and thus become important for very long times. The crossover in the reactive part of the shear viscosity from regular relaxation to a nonanalytic spec-

trum due to the long-time tail is examined. The observed suppression of the hydrodynamic long-time tail due to interference with structural relaxation corroborates a reasoning by Kirkpatrick and Nieuwoudt [30] for an apparent long-time tail seen in molecular-dynamics work [31]. These authors argued that the short-wavelength contributions of the cage effect lead to slow relaxation in dense liquids that obscure the appearance of the hydrodynamic long-time tails. In this paper, we gave a detailed quantitative explanation for the rapid suppression of the long-time anomaly in favor of the structural relaxation. The sensitive dependence of the cross-

over frequency on temperature makes a fine-tuning procedure necessary in order to observe the long-time-tail anomalies in supercooled liquids. Therefore it will be quite hard to observe the crossover from structural-relaxation dynamics to the long-time tail.

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