Interplay of orientational order and viscoelasticity in supercooled liquids near the glass transition

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The problem of the liquid-glass transformation continues to be a challenging one. It has been recently tackled by several high-powered theories such as mode-mode coupling. By contrast, the present model employs the intuitive picture of local orientational order in supercooled liquids and combines this with a variant of the Maxwell model of viscoelasticity. The resulting dynamic theory provides a simple scenario of how the viscosity of a supercooled liquid is enhanced due to its tendency to order orientationally. An important by-product is an expression for the glass-transition temperature in terms of the microscopic parameters of the theory, via which a connection with the formal, spin-glass theoretical approach can be established. The model leads to expressions for the dynamical modes in a supercooled liquid—quantities of direct experimental interest.

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I. INTRODUCTION

When a liquid is cooled adiabatically such that at every stage it is in thermal equilibrium with the environment, one obtains a crystalline solid. It is, however, not too difficult to cool a liquid rapidly yielding a supercooled phase. It is also quite easy to supercool a "computer" liquid. A supercooled liquid may eventually be trapped in a metastable state in which the nucleation rate approaches zero and the system appears frozen in a disordered solid state on any macroscopic time scale of measurement. This is often interpreted as a kind of continuous phase transition from liquid to glass [1]. The quantity that dramatically changes on supercooling as one approaches the glass transition is the viscosity. Its value rises from about 10^{-2} P for ordinary liquids to $10^{12} - 10^{13}$ P near a temperature T_G.

When a liquid is cooled at a finite rate ω_Q down to T_G, certain degrees of freedom of the system cannot relax to equilibrium but are *quenched* in a high-temperature configuration. Hence the glass transition is a nonequilibrium phenomenon as manifested, for example, in the dependence of T_G on ω_Q and in the change of the single-particle diffusive behavior from the Fickean to hoppinglike. As a result, supercooled liquids "appear to be liquid" only when probed at sufficiently low frequencies, but otherwise show elastic response.

The freezing-out of the motion in certain regions of the phase space makes the glass transition look somewhat similar to the transition in spin-glass alloys [2]. This has motivated the application of spin-glass theoretical techniques, e.g., quenched averaging, the replica trick, etc., to the problem of the glass transformation [3–7]. However, a crucial fact distinguishes ordinary glasses from spin glasses in that, unlike in the latter, there are no quenched impurities but certain "dynamically quenched" fluctuations which are "self-trapped" over macroscopic time scales. This view is supported by recent numerical investigations of apparent nonergodicity in ordinary glass-forming binary liquids [8–10].

Recent theories of glass transitions are based either on an atomistic level density-functional approach [11, 12] or the memory-function formulation [13, 14]. In the present approach we adopt the idea of *local orientational order* (LORO), due to Frenkel [15], and incorporate this into a dynamic theory. In LORO theory a dense liquid possesses local orientational order with high symmetries [16,17], not necessarily corresponding to those space-filling symmetries associated with crystals, but akin to icosahedral symmetries observed in quasicrystals [18]. The LORO can be pictured in terms of a "cage," which is a cluster of atoms positioned at the vertices of, say, a Voronoi polyhedron with the central atom at the origin whose diffusivity is thus severely restricted [19,20]. A similar description of a liquid had been used in the early days of neutron-scattering experiments [21]. In a somewhat obscure form, this picture is also implicit in the mode-coupling approach [13], when the structural relaxations—the α mode—are discussed.

The relevant information about the LORO is embodied in higher-particle distribution functions, e.g., the four-particle distribution $\rho_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$, for three-dimensional systems with pairwise spherically symmetric interactions [16,17]. How ρ_4 is described in terms of an orientational order parameter, a tensor of rank four or higher, has been the subject of our earlier work [22], henceforth refered to as I, and will be briefly reported in Sec. II. In I we have shown that the coupling between the local orientational variables and the deformation tensor leads to an internal stress which physically captures the

effect of the local misfit energy due to two misaligned cages. Our objective in this paper is to analyze the influence this internal stress has on the viscoelastic properties of a supercooled liquid [15]. To this end we introduce in Sec. III the concept of a rheological stress. We find that the tendency of the supercooled liquid to orientationally order itself (but being less likely to do so as the nucleation rate diminishes) leads to a large enhancement of the viscosity, which actually shows up as a divergence in our mean-field treatment [23]. This is discussed in Sec. IV. The theory developed here allows us to analyze in Sec. V the dynamical modes of the system, a necessary step towards calculating the dynamic structure factor [24]. Finally, our main conclusions and results are summarized in Sec. VI.

II. ORIENTATION-STRAIN COUPLING

The principal idea presented in I was that the basic entities of the theory are multiparticle distribution functions related to the probability of having at an arbitrary point $\mathbf{r}$ in the liquid, a local triad of vectors $\mathbf{h}_i$ ($i = 1, 2, 3$). These vectors define the local coordinates of a cage according to its orientation, and can be constructed in various ways, for example, by local Wigner-Seitz (or Voronoi) construction [25]. In a sense it is the averaged positions and orientations of the cage which are our dynamically quenched variables alluded to earlier. In accepting the notion of the cage we tacitly coarse-grain the system, avoiding the mathematical complexity of having to include short-wavelength modes in a proper hydrodynamic description [14]. Thus the main object in our theory should be the probability density $\rho(\mathbf{r}, \{\mathbf{h}_i\})$. For practical purposes this probability density can be expanded into a proper set of irreducible tensors of rank four or higher (Wigner matrices or similar) [19]. We shall denote them as $\Lambda^A(\mathbf{r})$, for the cage located at position $\mathbf{r}$; A may stand for four or six indices in order to describe cubic or icosahedral ordering, respectively [19,20]. As in other LORO liquid-state theories and also lattice models, we write the liquid Hamiltonian (coarse-grained free energy) as a quadratic functional of these tensors [26]. The orientational variables $\Lambda^A(\mathbf{r})$ are expected to couple to the local distortions of the liquid, as in "compressible" lattice models [27].

The considerations above yield the following form of the free-energy functional describing orientation-strain interactions [22]:

$$
\mathcal{F}\{\Lambda, \epsilon\} = \frac{1}{2V^2} \int d\mathbf{r}\, d\mathbf{r}'\, E_{AB}^0(\mathbf{r} - \mathbf{r}') \Lambda^A(\mathbf{r}) \Lambda^B(\mathbf{r}')
$$
$$
+ \frac{1}{2V^2} \int d\mathbf{r}\, d\mathbf{r}'\, G_{\alpha\beta}^{AB}(\mathbf{r} - \mathbf{r}') \Lambda^A(\mathbf{r}) \Lambda^B(\mathbf{r}') \epsilon_{\alpha\beta}(\mathbf{r})
$$
$$
+ \frac{1}{2V} \int d\mathbf{r}\, C_{\alpha\beta\gamma\delta} \epsilon_{\alpha\beta}(\mathbf{r}) \epsilon_{\gamma\delta}(\mathbf{r}). \tag{1}
$$

The first term in Eq. (1) accounts for pure orientational coupling between two cages centered at $\mathbf{r}$ and $\mathbf{r}'$ with the

strength E_{AB}^0. This term is known, in mean-field theory, to lead to a *first*-order phase transformation (when Λ's are treated, for example, as Potts variables) from the $\langle\Lambda\rangle = 0$ to the $\langle\Lambda\rangle \neq 0$ phase. The second term is the most crucial for our further analysis, for it describes the coupling between the orientational degrees of freedom and the local strain in the liquid, with the strength of interaction given by the tensor $G_{\alpha\beta}^{AB}$. Finally, the last term accounts for the elastic energy in conventional elasticity theories [28] in which $C_{\alpha\beta\gamma\delta}$ are the elastic coefficients:

$$
C_{\alpha\beta\gamma\delta} = \lambda \delta_{\alpha\beta}\delta_{\gamma\delta} + \mu(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}). \tag{2}
$$

Note that the λ and μ are the bare Lamé coefficients, the measured ones being dressed by the coupling between the fields Λ and ϵ. Throughout Eq. (1) we adopt the summation convention for tensor indices and use the symbol V for the volume of the system.

It is not customary to think in terms of a strain tensor in the liquid phase, but a viscoelastic liquid for which the cage concept is meaningful can be visualized as an isotropic elastic medium over appreciably long time scales. Thus if we were to employ equilibrium statistical mechanics, Eq. (1) would lead to a mean value of the strain in the liquid as in [22]:

$$
\langle\epsilon_{\alpha\beta}(\mathbf{r})\rangle = \frac{1}{V} \int d\mathbf{r}'\, K_{\alpha\beta\gamma\delta} G_{\gamma\delta}^{AB} \langle\Lambda^A(\mathbf{r})\Lambda^B(\mathbf{r}')\rangle, \tag{3}
$$

where $K_{\alpha\beta\gamma\delta}$ is the elastic compliance tensor (inverse of $C_{\alpha\beta\gamma\delta}$). Hence the thermodynamic value of the strain would be zero in the "disordered" liquid phase (corresponding to $\langle\Lambda\rangle = 0$) unless there is finite correlation between the cage orientations. The latter is a measure of short-range orientational order reminiscent of magnetic short-range order in an Ising paramagnet, that is to say, Λ's are like Ising spin variables, albeit much more complicated in view of their geometrical nature, but there is no conceptual difficulty in introducing them even in the liquid phase. In I we demonstrated how the jump in $\langle\Lambda\rangle$ and the Λ-Λ correlations of the type appearing in Eq. (3) cause several macroscopic quantitites, e.g., the total volume, the heat capacity, and the elastic compliance to change drastically as the liquid undergoes a transition to an orientationally ordered phase.

As we argued earlier our main task is to construct a dynamic theory associated with the free-energy functional in Eq. (1). Such a theory becomes unduly complex unless a certain simplified assumption concerning the orientational degrees of freedom is adopted. The assumption that captures the essential physics of the problem, we believe, is the one in which the local cages are permitted to have discrete orientations [19,20,22]. This allows us to visualize Λ^A as a p-state Potts variable, where $A = 1, 2, \ldots, p$. We need not specify the value of p; suffice it to note that even $p = 3$ is sufficient to account for most of the salient features of the problem, at least in the mean-field approximation [4,5]. Identifying the order parameter $\Psi(\mathbf{r})$ as that particular component of Λ^A which points toward the axis along which the cages would like to order, the free energy in Eq. (1) takes a simpler form:

$$\mathcal{F}\{\Psi, \epsilon\} = \frac{1}{2V^2} \int dr\, dr' \Delta E(\mathbf{r} - \mathbf{r}')\Psi(\mathbf{r})\Psi(\mathbf{r}')$$
$$+ \frac{1}{2V^2} \int dr\, dr' \Delta G_{\alpha\beta}(\mathbf{r} - \mathbf{r}')\epsilon_{\alpha\beta}(\mathbf{r})\Psi(\mathbf{r})\Psi(\mathbf{r}')$$
$$+ \frac{1}{V} \int dr\, C_{\alpha\beta\gamma\delta}\epsilon_{\alpha\beta}(\mathbf{r})\epsilon_{\gamma\delta}(\mathbf{r}'), \tag{4}$$

where ΔE and ΔG refer to the differences in the energy parameters between mutually parallel and perpendicular orientations of the cages [22].

To write down a kinetic relaxation equation for the orientational variables we imagine "orientational flips" in much the same manner as "spin flips" in kinetic Ising models [29,30]. These flips represent the reorientational motion of the cages due to interactions with other degrees of freedom. It is well known that in the linearized mean field theory the relaxational equation in the wave-vector space looks like [31]

$$\dot{\Psi}(\mathbf{q}, t) = -\nu(\mathbf{q})\Psi(\mathbf{q}, t)$$
$$+ \frac{\beta}{V\tau} \int d\mathbf{q}' \Delta G_{\alpha\beta}(\mathbf{q}')\Psi(\mathbf{q}', t)\epsilon_{\alpha\beta}(\mathbf{q} - \mathbf{q}', t). \tag{5}$$

The quantity $\nu(\mathbf{q})$ is the rate of relaxation associated with the pure orientational part of the free energy [viz. the first term in Eq. (4)], β is the inverse temperature in energy units, and τ is a parameter which sets the basic time scale of the relaxational processes induced by the heat bath; it is given a physical interpretation in Sec. III below. While earlier we did not specify any definite mechanism for this relaxation process, it is reasonable to imagine it to be such that if one of the local cages flips, the other must simultaneously undergo a reverse flip, which corresponds to the picture of supercooled liquids provided by computer simulations; see Ref. [17]. The particles leave their cage and get to another, which after a short time of internal rearrangements becomes a similar cage "pointing" in another "direction" leading to conserved kinetics for the orientational order parameter akin to the Kawasaki spin-exchange process in the kinetic Ising model [32]. This implies that $\nu(\mathbf{q})$ must vanish as $|\mathbf{q}| \to 0$ with the leading-order term in $\mathbf{q}$ proportional to $\mathbf{q}^2$. In fact, a mean-field analysis yields [33]

$$\nu(\mathbf{q}, T) = N\frac{\mathbf{q}^2\xi^2}{\tau}\left[1 - \frac{T_0}{T} + \frac{T_0}{T}R^2\mathbf{q}^2\right], \tag{6}$$

where N is the number of nearest-neighbor cages, ξ is the mean separation between them, and T_0 is the temperature at which the pure orientational order (no coupling to the remaining degrees of freedom) would occur. The quantity R is the typical range of interactions between the cages described by ΔE in Eq. (4).

The second term on the right-hand side of Eq. (5) represents the effect of cage reorientation resulting from the coupling to the translational degrees of freedom of the cages represented by the fluctuating strain tensor $\epsilon_{\alpha\beta}(\mathbf{q}, t)$. On the time scale over which this coupling is relevant it is permissible to replace the strain tensor by the (Hookean) stress tensor of the fluid, i.e., $\epsilon_{\alpha\beta} = K_{\alpha\beta\gamma\delta}\sigma_{\gamma\delta}$. Therefore we can rewrite Eq. (5) as [34]

$$\dot{\Psi}(\mathbf{q}, t) = -\nu(\mathbf{q})\Psi(\mathbf{q}, t)$$
$$+ \frac{\beta}{V\tau}K_{\alpha\beta\gamma\delta} \int d\mathbf{q}' \Delta G_{\alpha\beta}(\mathbf{q}')\Psi(\mathbf{q}', t)$$
$$\times \sigma_{\gamma\delta}(\mathbf{q} - \mathbf{q}', t). \tag{7}$$

III. VISCOELASTICITY

To establish a proper dynamical description of a supercooled liquid near T_G we develop a generalization of the Maxwell model of viscoelasticity theory. Recall that Maxwell constitutive relation interpolating between solid- and liquidlike behavior reads [15, 35]

$$\dot{\sigma}_{\alpha\beta}(t) = -\frac{1}{\tau}\sigma_{\alpha\beta}(t) + C_{\alpha\beta\gamma\delta}\dot{\epsilon}_{\gamma\delta}(t). \tag{8}$$

The quantity τ, the Maxwell relaxation time, determines the medium viscosity through the relation

$$\eta_{\alpha\beta\gamma\delta} = \tau C_{\alpha\beta\gamma\delta}. \tag{9}$$

Taking the frequency Fourier transform of Eq. (8) we have

$$\tilde{\sigma}_{\alpha\beta}(\omega) = i\eta_{\alpha\beta\gamma\delta}(\omega)\tilde{\epsilon}_{\gamma\delta}(\omega), \tag{10}$$

where [36]

$$\eta_{\alpha\beta\gamma\delta}(\omega) = \frac{\tau\omega C_{\alpha\beta\gamma\delta}}{1 + i\omega\tau}. \tag{11}$$

When the experimental probe frequency is much higher than the inverse of the Maxwell time, $\omega\tau \gg 1$, we obtain the stress-strain relation for a solid. For $\omega\tau \ll 1$, we observe viscous relaxation. In order to make the concept of the Maxwell model applicable to a liquid we shall work systematically in the wave-vector representation [24], thus $\tau = \tau(\mathbf{q})$.

Our strategy is to search for a mechanism that causes an enhancement of the Maxwell time τ so that the solidlike behavior persists over longer experimental time scales (i.e., smaller ω) leading to an increase in η when one supercools a liquid. The crucial point in making a connection between the Maxwell model and the formulation based on Eq. (1) is the observation that the presence of the local orientational order induces an internal stress tensor [cf. Eq.(3)], the physical origin of which has been discussed earlier:

$$\sigma_{\alpha\beta}^{\text{int}}(\mathbf{r}) = \frac{1}{V} \int dr' \Delta G_{\alpha\beta}(\mathbf{r} - \mathbf{r}')\Psi(\mathbf{r})\Psi(\mathbf{r}'). \tag{12}$$

Following the principle of superposition of stresses, which implies that the total stress in the system is additive, we have to replace the Maxwell constitutive relation, Eq. (8), by a generalized one which would lead to the proper superposition of stresses in either the low- or the high-frequency limit discussed earlier. To do so we introduce the concept of a rheological stress $s_{\alpha\beta}$, a quantity which measures the mismatch between the measured stress in the system $\sigma_{\alpha\beta}$, and the static stress tensor defined customarily as the functional derivative of the free energy Eq. (1) with respect to the strain [37]:

$$s_{\alpha\beta} = \sigma_{\alpha\beta} - \frac{\delta\mathcal{F}}{\delta\epsilon_{\alpha\beta}}. \tag{13}$$

Using the explicit form of $\mathcal{F}\{\Psi,\epsilon\}$ one easily finds that $s_{\alpha\beta}$ is indeed the difference between the measured stress and the internal stress given by Eq. (12) plus the elastic stress given by $\delta\mathcal{F}_{\rm el}/\delta\epsilon_{\alpha\beta}$.

When the local orientational degrees of freedom (the cages) get ordered the flow of the medium has to stop; thus we shall replace the Maxwell constitutive relation by

$$\dot{s}_{\alpha\beta} + \frac{1}{\tau(\mathbf{q})}s_{\alpha\beta} = -\frac{1}{\tau(\mathbf{q})}\frac{\delta\mathcal{F}_{\rm el}\{\epsilon\}}{\delta\epsilon_{\alpha\beta}}. \tag{14}$$

The relaxation time $\tau(\mathbf{q})$ in Eq. (14) is the main, bare time scale of all the relevant relaxation processes in our model. Therefore $\tau(\mathbf{q})$ has to be identified with the relaxation time [i.e., $1/\nu(\mathbf{q})$] associated with the bare kinetics of the local orientational order parameter $\Psi(\mathbf{q})$, Eq. (7).

Equation (14) is a constitutive relation, the use of which is not restricted to our current analysis. It can be employed in modeling other physical phenomena wherein the stress tensor is split in a natural way into two parts describing the long-wavelength behavior, and the other describing the short-wavelength behavior, for example, in the theory of coupling between accustic waves and thermal phonons [38].

It is convenient to rewrite Eq. (14) in terms of the measured stress, the internal stress, and the rate of strain tensor, thus

$$\frac{d}{dt}\left[\sigma_{\alpha\beta}(\mathbf{q},t) - \sigma_{\alpha\beta}^{\rm int}(\mathbf{q},t)\right]$$

$$+\frac{1}{\tau(\mathbf{q})}\left[\sigma_{\alpha\beta}(\mathbf{q},t) - \sigma_{\alpha\beta}^{\rm int}(\mathbf{q},t)\right] = C_{\alpha\beta\gamma\delta}\dot{\epsilon}_{\gamma\delta}. \tag{15}$$

In the absence of the internal stresses Eq. (15) reduces to the Maxwell constitutive relation Eq. (8) and it generalizes the constitutive equation proposed in Ref. [23].

To check that Eq. (15) leads to the required superposition of stresses for any frequency take the time Fourier transform of it leading to

$$\tilde{\sigma}_{\alpha\beta}(\mathbf{q},\omega) = \tilde{\sigma}_{\alpha\beta}^{\rm int}(\mathbf{q},\omega) + \frac{i\omega\tau(\mathbf{q})}{1 + i\omega\tau(\mathbf{q})}C_{\alpha\beta\gamma\delta}\tilde{\epsilon}_{\gamma\delta}(\mathbf{q},\omega). \tag{16}$$

For high frequencies Eq. (16) gives us solidlike stress superposition, i.e., $\sigma = \sigma^{\rm int} + \sigma^{\rm el}$, and the rheological stress $s_{\alpha\beta}$ vanishes. For low frequencies we obtain fluidlike behavior in which the rheological stress cancels the elastic contribution yielding

$$\tilde{\sigma}_{\alpha\beta} = \tilde{\sigma}_{\alpha\beta}^{\rm int} + i\omega\eta_{\alpha\beta\gamma\delta}(\mathbf{q})\tilde{\epsilon}_{\alpha\beta}, \tag{17}$$

where we have used the obvious generalization of the definition of viscosity from Eq. (9). As we shall show in what follows, the bare viscosity is renormalized due to the coupling with the orientational degrees of freedom in a fashion characteristic of the viscosity enhancement associated with the glass transformation.

IV. ORIENTATION CUM STRESS RELAXATION

We are now geared to investigate the coupling between the local orientational order and the remaining degrees of freedom in the system using the generalized viscoelastic model developed in Sec. III. At the outset we note that we will be interested primarily in the slow relaxational motion in the system; thus, for the time being, we shall not analyze the dynamic equation of motion for the current, but concentrate on the analysis of the constitutive relation. The dynamic equation for the orientational order parameter $\Psi(\mathbf{r})$ reads [cf. Eq. (7)]

$$\dot{\Psi}(\mathbf{q},t) = -\nu(\mathbf{q})\Psi(\mathbf{q},t)$$

$$+\frac{\beta}{\eta_0}\int d\mathbf{q}'\Delta G(\mathbf{q}')\Psi(\mathbf{q}',t)\sigma(\mathbf{q}-\mathbf{q}',t), \tag{18}$$

where we have dropped all the tensorial indices. In Eq. (18) we have used the definition of the bare viscosity Eq. (9), viz. $1/\eta_0 = K/\tau = 1/\tau C$.

Solving Eq.(18) and substituting it into the definition of the internal stress we obtain

$$\sigma^{\rm int}(\mathbf{q},t) = \frac{\beta}{\eta_0}\int d\mathbf{q}'\Delta G(\mathbf{q}')\int d\mathbf{q}''\int dt'\exp[-\lambda(\mathbf{q},\mathbf{q}',t-t')]\Delta G(\mathbf{q}'')\Psi(\mathbf{q}'',t')$$

$$\times[\Psi(\mathbf{q}-\mathbf{q}',t')\sigma(\mathbf{q}'-\mathbf{q}'',t') + \Psi(\mathbf{q}',t')\sigma(\mathbf{q}-\mathbf{q}'-\mathbf{q}'',t')], \tag{19}$$

with the initial condition $\sigma^{\rm int}(\mathbf{q},t=0) = 0$. For an interpretation of this particular initial condition, see the last paragraph of this section. In Eq. (19)

$$\lambda(\mathbf{q},\mathbf{q}') = \nu(\mathbf{q}) + \nu(\mathbf{q}-\mathbf{q}'). \tag{20}$$

Our aim now is to substitute Eq. (19) into Eq. (15) and consider the resulting equation, with an appropriate noise term added, as the Langevin equation for the stress tensor. For our purposes it is sufficient to calculate the averaged value of the stress tensor over the statistics of the noise. While carrying out this average (denoted by angular brackets) we encounter triple correlation functions of the sort $\langle\Psi(\mathbf{q}',t')\Psi(\mathbf{q}'',t')\sigma(\mathbf{q}-\mathbf{q}'-\mathbf{q}'',t')\rangle$. In handling these we make a random-phase-like decoupling resulting in

$$\langle\Psi(\mathbf{q}',t')\Psi(\mathbf{q}'',t')\sigma(\mathbf{q}-\mathbf{q}'-\mathbf{q}'',t')\rangle$$

$$= \langle\Psi(\mathbf{q}',t')\Psi(\mathbf{q}'',t')\rangle\langle\sigma(\mathbf{q}-\mathbf{q}'-\mathbf{q}'',t')\rangle. \tag{21}$$

Now, noting that the orientational order correlation function in Eq. (21) is an equal-time correlation and that the underlying stochastic process is assumed stationary and the system translationally invariant, we have

$$\langle\, \Psi(\mathbf{q}',t')\Psi(\mathbf{q}'',t')\,\rangle = \langle\,\Psi(\mathbf{q}')\Psi(\mathbf{q}'')\,\rangle\delta(\mathbf{q}+\mathbf{q}'')$$
$$= \chi(\mathbf{q}')\delta(\mathbf{q}'+\mathbf{q}''), \qquad (22)$$

where $\chi(\mathbf{q})$ is the "susceptibility" associated with the orientational order. Using now Eqs. (21) and (22), and substituting them into Eq. (19), we obtain the following expression for the averaged value of the internal stress tensor $\langle\sigma^{\text{int}}\rangle$:

$$\langle\sigma^{\text{int}}(\mathbf{q},t)\rangle = \beta\int_0^t dt' F(\mathbf{q},t-t')\langle\sigma(\mathbf{q},t')\rangle, \qquad (23)$$

where the memory kernel $F(\mathbf{q},t)$ is given by

$$F(\mathbf{q},t) = \frac{1}{\eta_0}\int d\mathbf{q}'\chi(\mathbf{q}')\Delta G(-\mathbf{q}')\exp[-t\lambda(\mathbf{q},\mathbf{q}')]$$
$$\times[\Delta G(\mathbf{q}')+\Delta G(\mathbf{q}-\mathbf{q}')]. \qquad (24)$$

Having this we may now solve Eq. (15) for the stress tensor using Laplace transforms. We obtain

$$\langle\tilde{\sigma}(\mathbf{q},z)\rangle = \frac{\tau(\mathbf{q})}{[1+z\tau(\mathbf{q})(1-\beta\tilde{F}(\mathbf{q},z)]}$$
$$\times[zC\langle\tilde{\epsilon}(\mathbf{q},z)\rangle - C\langle\epsilon(\mathbf{q},t=0)\rangle$$
$$+\langle\sigma(\mathbf{q},t=0)\rangle], \qquad (25)$$

where

$$\tilde{F}(\mathbf{q},z)$$
$$= \frac{1}{\eta_0}\int d\mathbf{q}'\frac{\chi(\mathbf{q}')\Delta G(-\mathbf{q}')[\Delta G(\mathbf{q}')+\Delta G(\mathbf{q}-\mathbf{q}')]}{z+\lambda(\mathbf{q},\mathbf{q}')}.$$
$$(26)$$

Equation (25) can be cast in a form exhibiting the renormalized Maxwell relaxation time $\tau_{\text{eff}}(\mathbf{q},z)$ as

$$\tau_{\text{eff}}(\mathbf{q},z) = \frac{\tau}{1-\beta\tilde{F}(\mathbf{q},z)}. \qquad (27)$$

In order to examine consequences of the renormalization of the relaxation time given by Eq. (27), it is instructive to rewrite Eq. (25) as

$$\langle\tilde{\sigma}(\mathbf{q},z)\rangle = \frac{1}{D(\mathbf{q},z)}\frac{\tau_{\text{eff}}(\mathbf{q},z)}{1+z\tau_{\text{eff}}(\mathbf{q},z)}$$
$$\times[zC\langle\tilde{\epsilon}(\mathbf{q},z)\rangle - C\langle\epsilon(\mathbf{q},t=0)\rangle$$
$$+\langle\sigma(\mathbf{q},t=0)\rangle], \qquad (28)$$

where

$$D(\mathbf{q},z) = 1 - \beta\frac{z\tau_{\text{eff}}(\mathbf{q},z)}{1+z\tau_{\text{eff}}(\mathbf{q},z)}\tilde{F}(\mathbf{q},z). \qquad (29)$$

Equation (27) is the main result of this section, which shows that within our mean-field-like analysis of coupled kinetics of the local orientational order and the stress in the viscoelastic regime, the generalized relaxation time diverges at the temperature T_G when

$$1 - \beta\tilde{F}(\mathbf{q},z) = 0. \qquad (30)$$

The relaxation processes under consideration are clearly important for low frequencies; in that regime

the memory function $\tilde{F}$ is essentially z independent. Equation (28) can now be analyzed in the limits when $z\tau_{\text{eff}}(\mathbf{q},z=0) \gg 1$ or $z\tau_{\text{eff}}(\mathbf{q},z=0) \ll 1$. The former applies when the temperature approaches the glass transition temperature defined by Eq. (27). In that case Eq. (28) describes the elastic response of the medium with the elastic coefficients enhanced by the factor $1/(1-\beta\tilde{F})$. In the low-frequency limit, Eq. (28) gives us the typical viscous stress-strain relation with the viscosity given by

$$\eta(\mathbf{q},z) = \frac{C/\tau}{1-\beta\tilde{F}(\mathbf{q},z)} = \frac{\eta_0}{1-\beta\tilde{F}(\mathbf{q},z)}, \qquad (31)$$

which can also be obtained using the Maxwell relation between the elastic coefficient and the viscosity. We conclude therefore that the rheological constitutive relation together with the kinetic model for the orientational degrees of freedom provide the necessary input to construct a kinetic theory for the liquid-glass transition.

Equation (30) immediately permits us to define the glass-transition temperature T_G as the one at which the zero-frequency long-wavelength component of the viscosity diverges. Hence

$$T_G = \frac{1}{\eta_0 k_B}\int d\mathbf{q}'\frac{\chi(T_G)\Delta G(-\mathbf{q}')[\Delta G(\mathbf{q}')+\Delta G(-\mathbf{q}')]}{\lambda(\mathbf{0},\mathbf{q}',T_G)},$$
$$(32)$$

where, following Eq.(20), $\lambda(\mathbf{0},\mathbf{q}') = \nu(\mathbf{q}')+\nu(-\mathbf{q}')$.

Equation (32) simplifies for systems with inversion symmetries, in which case

$$T_G = \int d\mathbf{q}\frac{\chi(\mathbf{q},T_G)[\Delta G(\mathbf{q})]^2}{\nu(\mathbf{q},T_G)}. \qquad (33)$$

The result (33) deserves close attention. The relaxation time $1/\nu(\mathbf{q})$, as defined in Eq. (6), depends on two temperatures T_G and T_0, the latter being a transition temperature for pure orienational model. The point is that one reaches T_G before reaching T_0. Combining now Eq. (32) with Eq. (6) we obtain an expression for the T_G in terms of the microscopic parameters of the model:

$$T_G = \frac{1}{Nk_B\eta_0\xi^2}\int dq\frac{\chi(\mathbf{q},T_G)[\Delta G(\mathbf{q})]^2}{1-\frac{T_0}{T_G}+\frac{T_0}{T_G}R^2\mathbf{q}^2}. \qquad (34)$$

This result, which follows from the present dynamical theory, should now be compared with that obtained from the theory of glass transition based on a spin-glass theory framework [5]. It was shown in Ref. [5] that the glass-transition temperature T_G is proportional to the variance of the quenched disorder arising from the assumption that the coupling coefficients $G_{\alpha\beta}$ in the free-energy functional Eq. (1), hence also ΔG's in Eq. (4) have fluctuating contributions. Although it is not possible to directly relate the various averages over the quenched disorder appearing in Ref. [5] with our more microscopic variables, the structure of both expressions for T_G turns out to be very similar. Indeed the right-hand side of Eq. (34) contains the square of the coupling coefficient between the orientational and elastic degrees of freedom and it is

tempting to identify this expression with the variance of quenched fluctuations (cf. Ref. [5]). This analogy can be further substantiated by noting that the assumed vanishing of the initial value of the internal stress tensor can be related to vanishing of $\Delta G(\mathbf{q})$, averaged in the sense of Ref. [5].

At this stage it may be pertinent to enquire about the role of the rate of cooling ω_Q in the theory. This question is admittedly a difficult one to answer satisfactorily, but we can nevertheless offer some speculation. When ω_Q is finite the particles of the liquid do not have time to adjust to their equilibrium positions, and hence it is not unreasonable to expect that the strength of the orientation-dependent interaction between cages should depend on ω_Q. As the quantities occurring under the integral in Eq. (34) all depend on this interaction, it is evident that the glass-transition temperature T_G would indeed be a function of the rate of cooling ω_Q.

In the following section we shall return to a discussion of the model and show how the enhancement of the viscosity predicted by Eq. (27) modifies standard expressions for measured quantities, such as longitudinal current correlation function and the dynamic structure factor.

V. DYNAMIC MODES

To study the consequences of the interplay between the local orientational order and the viscoelasticity on the hydrodynamic modes of the system we begin by writing down the usual set of conservation laws for the density and momentum in the wave-vector space as

$$\frac{\partial}{\partial t}\rho(\mathbf{q}, t) = iq^\alpha j^\alpha(\mathbf{q}, t),$$

$$\frac{\partial}{\partial t}j^\alpha(\mathbf{q}, t) = iq^\beta \Pi^{\alpha\beta}(\mathbf{q}, t), \tag{35}$$

where ρ is the fluid density, j^α is particle current, and $\Pi^{\alpha\beta}$ is the total stress tensor in the liquid containing hydrostatic pressure $-p(\rho)\delta^{\alpha\beta}$ and the kinematic $\sigma_{\text{kin}}^{\alpha\beta} = \rho j^\alpha j^\beta$ terms. In what follows we shall be interested in linearized hydrodynamics, therefore we shall neglect σ_{kin} (the so-called convective terms). Furthermore, we shall now linearize Eqs. (35) around $\rho = \rho_0 + \delta\rho$, ρ_0 being the uniform fluid density. Using $p(\rho) = p_0 + (\partial p/\partial\rho)_0\delta\rho = p_0 + \kappa_T\delta\rho$, where κ_T is the isothermal compressibility, and including the stress tensor of Sec. III in $\Pi_{\alpha\beta}$, we obtain

$$\frac{\partial}{\partial t}\delta\rho(\mathbf{q}, t) = iq_\alpha j_\alpha(\mathbf{q}, t),$$

$$\frac{\partial}{\partial t}j^\alpha(\mathbf{q}, t) = iq^\beta\left\{\kappa_T\delta^{\alpha\beta}\delta\rho(\mathbf{q}, t) + \sigma^{\alpha\beta}(\mathbf{q}, t)\right\}. \tag{36}$$

Taking the Laplace transform with respect to the time variable, we have

$$z\tilde{j}^\alpha(\mathbf{q}, z) + \frac{\kappa_T}{z}q^\alpha q^\beta\tilde{j}^\beta(\mathbf{q}, z) - iq^\beta\tilde{\sigma}^{\alpha\beta}(\mathbf{q}, z)$$

$$= j^\alpha(\mathbf{q}, 0) + i\kappa_T q^\alpha\delta\rho(\mathbf{q}, 0). \tag{37}$$

In order to analyze Eqs. (35) we shall use for $\sigma^{\alpha\beta}$ the rheological constitutive equation from Sec. III, namely Eq. (15). We should emphasize that all the hydrodynamic quantities appearing in this section are identified with the averaged values in the sense of Sec. IV. Thus from Eqs. (14) and (25)

$$\tilde{\sigma}^{\alpha\beta}(\mathbf{q}, z) = \frac{1}{D(\mathbf{q}, z)}\frac{\tau_{\text{eff}}(\mathbf{q}, z)}{1 + \tau_{\text{eff}}(\mathbf{q}, z)}$$
$$\times\{C^{\alpha\beta\gamma\delta}[z\tilde{\epsilon}^{\gamma\delta}(\mathbf{q}, z) - \epsilon^{\gamma\delta}(\mathbf{q}, t = 0)]$$
$$+ \sigma^{\alpha\beta}(\mathbf{q}, t = 0)\}. \tag{38}$$

On the other hand, recall that in the linearized theory

$$\dot{\epsilon}^{\alpha\beta}(\mathbf{q}, t) = (1/2\rho_0)i(q^\alpha j^\beta + q^\beta j^\alpha), \tag{39}$$

Combining Eqs. (38) and (39), and substituting in Eq. (37), we obtain the matrix equation for the current:

$$\mathcal{G}^{\alpha\beta}(\mathbf{q}, z)\tilde{j}^\beta(\mathbf{q}, z) = f^\alpha(\mathbf{q}, z), \tag{40}$$

where

$$\mathcal{G}^{\alpha\beta}(\mathbf{q}, z) = \left[z^2\delta^{\alpha\delta} + \kappa_T q^\alpha q^\delta \right.$$
$$\left. + \frac{z\tau_{\text{eff}}(\mathbf{q}, z)}{1 + z\tau_{\text{eff}}(\mathbf{q}, z)}\frac{C^{\alpha\beta\gamma\delta}q^\gamma q^\delta}{\rho_0 D(\mathbf{q}, z)} \right] \tag{41}$$

and

$$f^\alpha(\mathbf{q}, z) = z\left[j^\alpha(\mathbf{q}, 0) + i\kappa_T q^\alpha\delta\rho(\mathbf{q}, 0) \right.$$
$$\left. + i\frac{z\tau_{\text{eff}}(\mathbf{q}, z)}{1 + z\tau_{\text{eff}}(\mathbf{q}, z)}\frac{\sigma^{\alpha\beta}(\mathbf{q}, 0)q^\beta}{D(\mathbf{q}, z)} \right]. \tag{42}$$

As is evident from Eq. (42) the right-hand side of Eq. (40) contains the initial values of all the relevant quantities.

Equation (40) is the central result of this section. The poles of the matrix $\mathcal{G}^{-1}$, $z = z(\mathbf{q})$ determine the hydrodynamic modes of the system. Note that $\tilde{j}_\alpha(\mathbf{q}, z)$ determines the relaxation of the macroscopic current, with an arbitrary initial condition. Hence, by the Onsager regression hypothesis, the long time decay of the long-wavelength component of equilibrium current fluctuations, described by the correlation function $\tilde{\mathcal{J}}(\mathbf{q}, z)$, is also governed by the matrix $\mathcal{G}^{-1}$.

Consider first the high-frequency regime discussed in Sec. IV. In that limit the matrix $\mathcal{G}$ simplifies and one obtains the usual expression for the dynamical matrix of an elastic medium with enhanced elastic coefficients. Indeed using the expression for the elastic coefficient tensor of an isotropic medium Eq. (2), one obtains expressions for the frequencies of the longitudinal and transverse waves

$$\omega_\| = q\sqrt{\kappa_T + \frac{1}{\rho_0}\left(\frac{\lambda + 2\mu}{1 - \beta\tilde{F}}\right)}, \tag{43}$$

$$\omega_\perp = q\sqrt{\frac{1}{\rho_0}\frac{\mu}{1 - \beta\tilde{F}}}.$$

Note the occurrence of the denominator $1 - \beta\tilde{F}$ in Eq. (43)

indicating an increase of the rigidity of the supercooled liquid when the temperature approaches T_G.

In the opposite limit of low frequencies the system dynamics becomes fluidlike with enhanced viscosity. For an interesting case of transverse waves we obtain

$$\omega_\perp = -iq^2 \frac{\eta_0}{1 - \beta \tilde{F}}, \tag{44}$$

the imaginary i indicating the diffusive character of these modes.

In a similar fashion we can write down expressions for the longitudinal and transverse current correlation functions, which appear to be essentially the same as in Ref. [24], provided the values of the elastic coefficients and the viscosities are modified by the correlations due to coupling to the local orientational degrees of freedom in the manner described above.

VI. CONCLUSIONS

The mean-field analysis of the combined viscoelasticity and local orientational order presented in the preceding sections shows how the kinetic effects associated with the orientational ordering in the supercooled liquid lead to enhancement of the fluid viscosity and the elastic moduli of the system as the glass transition is approached from above. The crucial role in the model is played by the renormalized Maxwell relaxation time τ_{eff} given by Eq. (27). The fact that τ_{eff} increases when one approaches the glass-transition temperature implies that the viscous behavior of the system would be observed only after waiting for a time much longer than in the "high-" temperature fluid, for example, near the triple point. The enhancement of the Maxwell time explains why one can use a crude model of the glass in which the translational degrees of freedom of the system are treated as in an elastic medium. Our results also show that the sluggishness of the system manifests itself in the increase in *both* viscosity and elastic moduli as one approaches T_G.

The mean-field analysis presented here suffers from several shortcomings. For example, it predicts the divergence of the relaxation time at the transition. A more refined analysis would remove this defect of theory, though at the expense of considerable calculational complexity which, we believe, will not add much to the perceived physical picture. Also our model analysis pre-

dicts an identical rate of increase of the viscosity and the Maxwell time, when one approaches T_G. This result also will be modified in a more refined treatment. Recall how a considerable "background" viscosity arises in the mode-coupling theory of a liquid near the critical point.

The glass transition is often thought to be essentially kinetic in nature. In view of this it is indeed consistent that the transition temperature predicted by our present model, viz. Eq. (34), correlates with the previous result for the glass-transition temperature obtained by the use of the spin-glass theory [5]. The quenched averages and replica tricks were used in Ref. [5] to mimic the nonequilibrium nature of the glass transformation. In the present approach this is achieved by proposing a fully dynamic model with specific kinetics of the local orientational order parameter.

The important ingredient of our model is the concept of the rheological stress, Eq. (13), and the rheological constitutive relation, Eq. (14). We believe that these concepts have a much wider application than envisaged in the present treatment. The rheological stress can also be used in analyzing the properties of such systems for which a clear classiffication of different groups of degrees of freedom can be made based on the considerations of space-time and "internal" symmetries. The possible examples that immediately come to mind are compressible magnetic systems, polymers, deformable dielectrics, etc. in which our ideas can be tested.

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