Solidity of viscous liquids. V. Long-wavelength dominance of the dynamics

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This paper is the fifth in a series exploring the physical consequences of the solidity of glass-forming liquids. Paper IV proposed a model where the density field is described by a time-dependent Ginzburg-Landau equation of the nonconserved type with rates in k space of the form $\Gamma_0 + Dk^2$. The model assumes that $D \gg \Gamma_0 a^2$ where $a$ is the average intermolecular distance; this inequality expresses a long-wavelength dominance of the dynamics which implies that the Hamiltonian (free energy) to a good approximation may be taken to be ultralocal. In the present paper we argue that this is the simplest model consistent with the following three experimental facts: 1) Viscous liquids approaching the glass transition do not develop long-range order; 2) The glass has lower compressibility than the liquid; 3) The alpha process involves several decades of relaxation times shorter than the mean relaxation time. The paper proceeds to list six further experimental facts characterizing equilibrium viscous liquid dynamics and shows that these are readily understood in terms of the model; some are direct consequences, others are quite natural when viewed in light of the model.

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I. INTRODUCTION

The idea that viscous liquids approaching the calorimetric glass transition are solid-like goes back in time at least to Kauzmann’s and Goldstein’s famous papers from 1948 and 1969 [1, 2]. According to these authors, when a molecule changes position in a highly viscous liquid, it happens in the form of a “flow event,” a sudden rearrangement of a group of molecules. In this picture, which was later confirmed by computer simulations, all motion is vibrational in the time between flow events. This indicates that a viscous liquid is like a disordered solid, albeit one that is able to flow over long times.

The property that highly viscous liquids are solid-like and more to be viewed as “solids that flow” than like ordinary less-viscous liquids, is here termed “solidity.” This paper is the fifth in a series (I-IV) [3, 4, 5, 6] devoted to extracting the physical consequences of the solidity of highly viscous liquids. An extensive discussion of solidity, its motivation and consequences, may be found in the introduction to paper IV to which the reader is referred for further physical background.

A crucial ingredient of solidity is time-scale separation in the equilibrium viscous liquid. This is the fact that while some processes occur on the vibrational time scale, i.e., in the picoseconds range, the genuine relaxation processes are much, much slower. Depending on temperature the latter processes occur on time scales of milliseconds, second, days,... The below discussion focuses exclusively on modelling the slow, relaxational processes.

The first paper from our group utilizing arguments from solid-state elasticity preceded this series. This was a joint publication with Olsen and Christensen where the “shoving model” for the temperature dependence of the viscosity (or relaxation time) was proposed [7]. According to this and related “elastic” models [8, 9] the activation energy is proportional to the instantaneous shear modulus $G_\infty$ (i.e., measured on a very short time scale and thus corresponding to the solid state defined by a potential energy minimum). This elastic constant increases significantly upon cooling, in fact enough to explain the observed non-Arrhenius behavior for several molecular liquids [7, 8, 9] (more data are needed to investigate whether this generally explains the non-Arrhenius viscosity).

The first and second papers of the series focussed on the flow events themselves (I,II). In paper I a “solidity length” $l$ was introduced that defines the length scale below which there is time to establish elastic equilibrium between two flow events. In terms of the average intermolecular distance $a$, the alpha relaxation time $\tau$, and the high-frequency sound velocity $c_\infty$, the solidity length is given by $l^4 = a^3 \tau c_\infty$. Close to the calorimetric glass transition the solidity length approaches 1 $\mu$m. Thus a glass-forming liquid is solid-like on quite large length scales. The model discussed in IV and the present paper focuses on the dynamics below the solidity length.

Papers III and IV [5, 6] dealt with the alpha relaxation process and how to explain its seemingly generic high-frequency loss $\propto \omega^{-1/2}$ [10]. Paper III approached the problem inductively by noting that the old BEL model from 1967 [11] fits data for the frequency-dependent shear modulus well. Starting from the BEL model it was argued that the $\omega^{-1/2}$ high-frequency behavior arises from a long-time tail mechanism operating over a range of times shorter than the alpha relaxation time. This was justified by a solidity-based argument with the irrelevance of momentum conservation as an important ingredient, thus allowing for the centre of mass to move following a flow event. As detailed in Refs. [12, 13] momentum conservation is irrelevant for highly viscous liquids, just as it is irrelevant in theories of defect motion in crystals.

Paper IV and Ref. [14] took a deductive approach and proposed a field-theoretic model giving a concrete realiza-
In the present paper, the generic $\omega^{-1/2}$ high-frequency decay of the alpha loss derives from a third-order term in the Hamiltonian (free energy). The model of paper IV, besides regarding momentum conservation as irrelevant just as in other stochastic models (e.g., of polymer dynamics \cite{13}), was based on the observation that even density conservation is apparently disobeyed on the alpha time scale. This also follows from solidity: A flow event brings the liquid from one to another potential energy minimum. Any potential energy minimum corresponds to a state of elastic equilibrium, thus a state of zero divergence of the stress tensor – a “solid” state. From the standard equations of elasticity \cite{10} it follows that upon a local density change, the leading term in the displacement field in the surroundings is radial and varies with distance $r$ from the flow event as $1/r^2$. This is a pure shear displacement, implying that in a coarse-grained description density can change at one point without changing elsewhere: Density has the appearance of not being conserved. This idea may be summarized into the following equation for the density dynamics, where $b_\mu$ is a dimensionless measure of the magnitude of the flow event taking place at $r_\mu$ at time $t_\mu$:

$$\dot{\rho}(r,t) = \sum_\mu b_\mu \delta(r-r_\mu)\delta(t-t_\mu). \tag{1}$$

Equation (1) does not constitute a *theory*, of course, since it does not describe how different flow events correlate; it just gives a coarse-grained *description* of the equilibrium density fluctuations. Nevertheless, Eq. (1) serves to emphasize that density has the appearance of not being conserved, a result which is less trivial than the already-mentioned momentum nonconservation that derives directly from the extremely large kinematic viscosity (transverse momentum diffusion constant) \cite{17} that any liquids acquires upon approaching the calorimetric glass transition. The model discussed in IV and below incorporates the main idea behind Eq. (1), density nonconservation, but the model is explicitly consistent with statistical mechanics, and its description of the density dynamics is more involved than that of Eq. (1).

In the present paper, supplementing the arguments of papers III and IV, we adopt a combined *inductive/deductive* approach. First, we list three fundamental facts characterizing viscous liquids from which the model is arrived at; this constitutes the *inductive* part (Secs. 2 and 3). We then proceed to discuss six further fundamental facts and their relation to the model (Sec. 4). Some of these are consequences of the model; others just appear quite natural when viewed in light of the model. This constitutes the *deductive* part of the paper.

II. THREE FACTS OF VISCOUS LIQUID DYNAMICS

In this section three facts characterizing glass-forming liquids approaching the calorimetric glass transition are listed.

- **Fact 1:** *There is no long-range density-coupled order*

One approach to understanding why the viscosity increases ten orders of magnitude for a temperature decrease of often just 10-15% is to assume that some long-ranged order develops upon continued supercooling. Indeed, according to a number of popular models the dramatic relaxation time increase is a consequence of the liquid approaching a critical point where the relaxation time becomes infinite (see, e.g., the recent interesting papers by Tanaka and their useful list of references \cite{18}). In line with the theory of critical phenomena it is commonly assumed that there is a diverging correlation length at the critical point. There is no consensus, however, on how to define the proposed diverging correlation length, i.e., which quantity develops long-ranged correlations. Numerous X-ray and neutron scattering correlation length, that whatever this hypothetical quantity may be, it does not couple to the density field.

- **Fact 2:** *The glassy phase has lower compressibility than the liquid phase.*

“Compliance-type” linear-response quantities like specific heat, compressibility, and thermal expansion coefficient all decrease when going from the liquid to the glassy phase. There are no known examples where they increase upon entering the glassy phase. The glass transition is a falling-out-of-equilibrium taking place when the liquid relaxation time becomes longer than the characteristic laboratory time scales. Suppose, as is commonly assumed, that each compliance-type linear-response quantity has contributions from both the fast (vibrational) and the much slower configurational degrees of freedom. Then the linear-response quantities must decrease at the glass transition, because below $T_g$ the configurational degrees freeze and cease to contribute. In particular, the compressibility decreases. This is fact 2.

- **Fact 3:** *The alpha process is characterized by a distribution of relaxation times covering several decades of times shorter than the alpha relaxation time.*

Dielectric relaxation experiments are often fitted by the frequency-dependent response function corresponding to a stretched exponential dipole autocorrelation function, $\exp[-(t/\tau)^\beta]$, where typical values of $\beta$ lie in the interval 0.3-0.7. This reflects the fact that viscous liquids almost without exception do not have simple exponential autocorrelation functions of the relevant quantities:
III. THE SIMPLEST MODEL FOR EQUILIBRIUM VISCOUS LIQUID DYNAMICS CONSISTENT WITH FACTS 1-3

In this section we ask: Which variable(s) must be included in any useful theory? What are the simplest dynamics for this/these variable(s) consistent with facts 1-3? Most models for viscous liquid dynamics attempt to explain both temperature- and time-dependence, i.e., both the non-Arrhenius average alpha relaxation time and the alpha relaxation linear-response characteristics. We here leave aside the non-Arrhenius problem (although solidity seems to play an important role even here[8]) and focus only on describing the thermal equilibrium fluctuations at a given temperature. The non-Arrhenius behavior is easily subsequently incorporated into the model by hand since the model parameters may by arbitrary functions of temperature.

Most of physics – from particle physics to critical phenomena, electromagnetism, many-body theory, and condensed-matter theory in varying contexts – is nowadays formulated in the language of field theory. It is natural to expect that viscous-liquid dynamics should also be described by a field theory. The question which variables are relevant thus becomes: “Which fields must be included in the description?”

The obvious fields are those of standard hydrodynamics: the momentum, energy, and particle density fields. As mentioned, the conservation laws for momentum and energy are both irrelevant for viscous liquids [12] [13]. Thus the standard hydrodynamic description based on continuity equations looses its physical significance. Despite the fact that solidity also implies apparent density nonconservation, the situation is different for the particle density field – after all, molecules are not continuously exchanged with the surroundings as momentum and energy are. We thus base the model sought for on the density field $\rho(r, t)$. The question which other fields that should be included to have a complete description of the macroscopic dynamics, is dealt with briefly at the end of this section.

The next question is: What are the simplest possible dynamics? Density dynamics of viscous liquids have two parts, vibrations (phonons) and a “relaxing” part of the dynamics. At low temperatures the alpha relaxation time is much larger than picoseconds, and the two dynamics are well separated. This implies that it makes good sense to ignore the vibrational part of the dynamics.

Assuming that the relevant field theory is based on a Hamiltonian (i.e., a free energy functional), the question is now how to model the “relaxing” dynamics consistent with the Hamiltonian. The answer to this is well-known: use Langevin dynamics. The Langevin equation is the canonical way to arrive at dynamics from statics [13, 20, 21, 22]. If the relevant variables are denoted by $Q_1, ..., Q_n$, the Hamiltonian is $H(Q_1, ..., Q_n)$, and $\beta = 1/k_B T$, the Langevin equation is

$$\dot{Q}_i = -\gamma_i \partial_i (\beta H) / \partial Q_i + \xi_i(t)$$

with $\xi_i(t)$ a Gaussian white noise term with zero mean obeying $\langle \xi_i(t) \xi_j(t') \rangle = 2\gamma_i \delta(t - t')$. These equations imply that the canonical probabilities $\alpha \exp(-\beta H)$ are reproduced, ensuring consistency with statistical mechanics [13, 20, 21, 22].

Recall that if the system consists of $N$ molecules with coordinates $r_j$ in volume $V$, the density field is defined by $\rho(r) = \sum_j \delta(r - r_j)$. As always when there is translational invariance it is convenient to go to k-space: the range of allowed k-vectors is limited to the discrete set consistent with periodic boundary conditions. We define the $k$th density component as

$$\rho_k = \frac{1}{\sqrt{N}} \sum_j e^{i k \cdot r_j}.$$  

With this normalization the $\rho_k$ fluctuations become independent of $V$ for $V \to \infty$ ($N/V = $ Const.) and the static structure factor $S(k)$ is given by $S(k) = \langle \rho_k \rho_{-k} \rangle$ ($V \to \infty$). If $\Gamma_k$ is the rate of the $\rho_k$ dynamics, the Langevin equation [13, 20, 21, 22] is

$$\dot{\rho}_k = -\Gamma_k \frac{\partial (\beta H)}{\partial \rho_k} + \xi_k(t).$$  

The complex noise term obeys $\xi_k^*(t) = -\xi_{-k}(t)$ and $\langle \xi_k(t) \xi_{k'}(t') \rangle = 2\Gamma_k \delta(t - t')$. Equation (3) is a standard time-dependent Ginzburg-Landau equation. Because $\rho^*_k = \rho_{-k}$ this equation in conjunction with the $\rho_{-k}$ equation are equivalent to two real Langevin equations, one for the real part of $\rho_k$ and one for its imaginary part.

Following standard field theory procedure we split $H$ into a sum of a quadratic “free-field” term $H_0$ and an “interaction” term $H'$ containing the third and higher-order terms:

$$H = H_0 + H'.$$  

Regarding $H'$ as a perturbation, we focus on the dynamics embodied in the free-field time-autocorrelation function denoted by $\langle \rho_k(0) \rho_{-k}(t) \rangle_0$. If there were no
higher order terms, because \( S(k) = \langle \rho_k \rho_{-k} \rangle \) the free-field Hamiltonian would be

\[
\beta H_0 = \frac{1}{2} \sum_k \frac{\rho_k \rho_{-k}}{S(k)}. \tag{5}
\]

Substituting this into Eq. (3) we find that the free-field time-autocorrelation function \( \langle \rho_k(0) \rho_{-k}(t) \rangle_0 \) is an exponential with decay rate \( \gamma_k \) given by

\[
\gamma_k = \frac{\Gamma_k}{S(k)}. \tag{6}
\]

When \( H' \) is regarded as a perturbation, the distribution of relaxation times is roughly given by the distribution of \( \gamma_k \)’s.

Since molecules cannot disappear, one would a priori assume \( \Gamma_k \propto k^2 \) (“conserved” case – model B of Ref. [23]), reflecting the expectation that density at sufficiently long wavelengths obeys a diffusion equation. Because the static structure factor \( S(k) \) has a non-zero limit as \( k \to 0 \), however, \( \Gamma_k \propto k^2 \) implies that density fluctuations become slower and slower at larger and larger wavelengths (Eq. (5)), which is inconsistent with fact 2: At the glass transition the liquid high-frequency compressibility becomes the glass compressibility. Fact 2 states that this quantity is lower than the liquid (dc) compressibility, implying that there are relaxational volume fluctuations on a macroscopic length scale in the equilibrium liquid; this is also directly known from measurements of the frequency-dependent bulk modulus showing that the low-frequency bulk modulus is lower than the high-frequency [24]. Thus density fluctuations cannot be described by \( \Gamma_k \propto k^2 \) as \( k \to 0 \), and density must have the appearance of a non-conserved field.

Given that \( \Gamma_k \propto k^2 \) does not work, the simplest alternative is that \( \Gamma_k \) is independent of \( k \); \( \Gamma_k = \Gamma_0 \) (“non-conserved” case – model A of Ref. [22]). This, however, also does not work for the following reason. For \( ka \approx 1 \) the static structure factor \( S(k) \) is of order one, whereas for \( k \to 0 \) \( S(k) \) converges to the ratio between liquid compressibility and that of an ideal gas at the same density. This ratio is typically somewhat larger than \( 10^{-2} \). Thus if \( \Gamma_k = \Gamma_0 \), Eq. (5) would imply a range of relaxation times covering at most 2 decades. This is inconsistent with fact 3.

Since \( \Gamma_k \propto k^2 \) contradicts fact 2 and \( \Gamma_k = \Gamma_0 \) contradicts fact 3, the next possibility is a combination of the two:

\[
\Gamma_k = \Gamma_0 + Dk^2. \tag{7}
\]

For this expression to be consistent with experiment the coefficient \( D \) must be quite large: Unless the \( Dk^2 \) term for the range of allowed \( k \)-vectors makes \( \Gamma_k \) vary several decades, the model won’t work for the same reason that \( \Gamma_k = \Gamma_0 \) doesn’t work. Since the maximum \( k \) obeys \( ka \sim 1 \), this means that the following inequality must apply:

\[
D \gg \Gamma_0 a^2. \tag{8}
\]

The inequality (8) expresses a crucial long-wavelength dominance of the dynamics because it implies that the \( Dk^2 \) term dominates the rate expression Eq. (7) for a range of small \( k \) vectors corresponding to wavelengths much larger than \( a \). Note that, whereas in papers III and IV this inequality was justified by microscopic arguments, it here comes about from a search for the simplest possible model consistent with facts 1-3.

In conjunction with fact 1, long-wavelength dominance of the dynamics implies that static (equal-time) correlations of density fluctuation at differing points are of little importance when it comes to their influence on the dynamics. Consequently, in the name of simplicity such correlations will be assumed to be absent altogether. A field theory with no equal-time correlations between fields at different points in space is termed “ultralocal” [23]. In \( k \)-space the assumption of ultralocality means that all coefficients are \( k \) independent in the expansion in orders of \( \rho_k \): \( H_0 = \sum_k (1/2A) \rho_k \rho_{-k} \) and \( H' = \sum_{k,k'} (\lambda_3/3\sqrt{N}) \rho_k \rho_{-k} \rho_{-k'} + \ldots \). Note that the fact that equal-time density fluctuations are uncorrelated in space does not mean that the entire model is trivial – there are still non-zero correlations between density fluctuations at different positions at different times. The situation is analogous to a trivial spin model (no spin-spin interactions) with Kawasaki dynamics where a spin flip at one point can take place only if a neighboring spin flips in the opposite direction. If by chance a given up spin is surrounded by a large island of only up spins, the given spin will be frozen for some time; thus the dynamics of this spin is influenced by those of its surrounding spins even though there are no equal-time spin-spin correlations.

A theory for viscous liquid dynamics should as a minimum make it possible to calculate all macroscopic \( k \)-dependent linear-response quantities. Calculation of response functions via the fluctuation-dissipation theorem involves autocorrelation functions of variables like the dipole density (dielectric constant), bulk modulus (pressure), shear stress (shear modulus), and energy density (specific heat). Note that the \( k \)-dependent bulk modulus may be determined from density fluctuations alone, and thus pressure (basically the trace of the stress tensor) is not an independent variable.

These considerations lead to the following recipe (IV):

1. The relevant degrees of freedom are fields \( \phi^{(1)}(r), \ldots, \phi^{(n)}(r) \) defined as: a) the densities of the different molecules, b) the densities of the molecules’ various configurational variables reflecting the molecular symmetry, c) the 5 stress tensor fields of the traceless stress tensor, d) the potential density energy field;
2. The Hamiltonian $H$ (free energy) is ultralocal and consists of various invariant (i.e., scalar) terms;

3. For each field the dynamics are described by a time-dependent Ginzburg-Landau equation, i.e., a Langevin equation of the form
   
   $\phi^{(j)}_k = -\Gamma_k^j \frac{\partial (\beta H)}{\partial \phi^{(j)}_k} + \zeta^j_k(t)$,

   where $\zeta^j_k(t)$ is a standard Gaussian white noise term;

4. For each density field the Langevin equation rates are given by $\Gamma_k^j = \Gamma_0^j + D^j k^2$, where $D^j \gg \Gamma_0^j a^2$, for all other fields the rates are k-independent: $\Gamma_k^j = \Gamma_0^j$.

Including the extra fields into the model makes it possible to calculate the frequency-dependent dielectric constant and shear modulus, as well as the 8 fundamental frequency-dependent thermoviscoelastic response functions [24]: the isochoric and isobaric specific heats, the isothermal and adiabatic compressibilities, the isobaric expansion coefficient, the adiabatic contraction coefficient, the isochoric and adiabatic pressure coefficients.

IV. SOME FURTHER FACTS OF VISCOUS LIQUID DYNAMICS AND THEIR INTERPRETATION IN LIGHT OF THE MODEL

Below are listed six experimental facts that are each nontrivial in the sense that there is no logically compelling connection between it and facts 1-3. Nevertheless, when viewed in light of the model, the facts appear natural. For each fact we detail it, argue that it is nontrivial, and discuss how it relates to the model.

- **Fact 4**: Below the alpha-loss peak frequency the loss virtually follows the Debye prediction, i.e., is proportional to $\omega$. Thus there is a rather sharp cut-off at long times in the relaxation time distribution.

The alpha loss peaks, which are typically measured by dielectric relaxation experiments, are always asymmetric towards the high-frequency side. At low frequencies they quite well follow the Debye prediction $[\propto 1/(1+i\omega \tau)]$, i.e., the loss is virtually proportional to frequency; the same applies, e.g., for the frequency-dependent shear modulus. This implies that, if the linear response is written formally as a sum of Debye processes, there is a cut-off at long times in the relaxation-time distribution. In the time domain a Debye process corresponds to a simple exponential dipole autocorrelation function, and the long-time cut-off implies that at long times the autocorrelation function decays exponentially fast to zero.

Given the spatial disorder of any viscous liquid it is not surprising that Debye peaks are rarely observed, but the effective cut-off at long relaxation times is a highly nontrivial experimental fact. If the non-Debye relaxation were due to effects of disorder-induced activation-energy broadening, the obvious guess would be some Gaussian activation-energy distribution. This, however, implies loss peaks that are symmetric in a log-log plot which is inconsistent with experiment.

Because there is a minimum relaxation rate ($\Gamma_0$), the model predicts a long-relaxation time cutoff (and thus asymmetric loss peaks stretching to high-frequency side). Of course one might argue that the long-time cut-off was built into the model via Eq. (7). The point we wish make is that this equation was not justified from fact 4, but as the simplest way to rationalize facts 1-3. Fact 4 follows.

- **Fact 5**: Above the alpha loss peak frequency the loss appears to be generically close to $\omega^{-1/2}$.

Above the alpha loss peak frequency the loss decays following an approximate power law $\propto \omega^{-\nu}$ where the exponent is typically between 0.3 and 0.7. The shape of the loss peak often changes with temperature, i.e., temperature superposition (TTS) is often not obeyed. It is now generally agreed that Johari-Goldstein beta processes may be found at much lower frequencies than previously thought [27]. Thus, since alpha and beta relaxations have quite different temperature dependence, low-lying beta processes easily lead to TTS violations even in the Hertz regime and below. According to this reasoning the “generic” characteristics of the alpha process is observed only when TTS is accurately obeyed. A study of the dielectric loss of 10 molecular liquids published in 2001 [10] indicated that when TTS is accurately obeyed, the exponent $\nu$ is close to 1/2. This was recently confirmed from a much more detailed study involving more than 40 different liquids [28]. As shown in Ref. [14] paper IV to lowest order in perturbation theory a third-order term in the model Hamiltonian implies that the loss varies $\propto \omega^{-1/2}$ for $\omega$’s higher than the loss peak frequency.

- **Fact 6**: The alpha relaxation process is dominated by small-angle jumps.

Many models assume “cooperatively rearranging regions” that do not interact with one another. In this spirit the simple picture of the dynamics as made up of discrete, well-defined and localized flow events implies that molecules either move significantly (those involved in the flow event) or do not move at all (those in the surroundings). Thus molecular jumps are expected typically to be fairly large and molecular orientations would be expected to change considerably during a jump. The molecular jump angles cannot be probed by linear-response experiments, but fortunately they can by NMR experiments. The surprising result of Böhmer and coworkers [29, 30] is that small-angle jumps dominate.

This observation calls for an explanation in terms of solidity: The reason that small angle jumps dominate must
be that – if the flow event picture is not completely wrong – the small adjustments in the surroundings required to reestablish elastic equilibrium dominate the overall picture. In fact, a simple solidity-based calculation (I) shows that the jump-angle distribution \( P(\phi) \) varies as \( 1/\phi^2 \) (this distribution is not normalizable because there are infinitely many molecules in the surroundings – in reality the distribution is cut-off at very small angles due to the fact that elastic effects do not propagate beyond the solidity length). This distribution clearly gives largest weight to the small jump angles.

When viewed in light of the model it should be recalled that the crucial \( \Gamma_0 \neq 0 \) assumption expressing apparent density nonconservation can come about only if a flow event is followed by the small solidity-based adjustments of molecular positions in the far surroundings. Thus fact 6 fits nicely with \( \Gamma_0 \neq 0 \).

- **Fact 7:** Viscous slowing down is not accompanied by significant changes in the static structure factor.

As mentioned, a popular and obvious explanation of the dramatically increasing relaxation time for liquids approaching the calorimetric glass transition is that this comes from a build-up of some sort of long-range order, possibly signalling that there is a critical point not far below \( T_g \) where the relaxation time becomes infinite. As also mentioned, numerous experiments have looked for long-range order, but found none. Not only is there no long-range order, but the liquid structure as probed by \( S(k) \) via X-ray or neutron scattering experiments changes little over the temperature range where the relaxation time changes by 10 or more orders of magnitude. It is matter of taste whether or not one regards this as surprising [31].

The model does not deal with the temperature dependence of the alpha relaxation time (determined by the model parameter \( \Gamma_0 \)). The very fact that the structure does not exhibit long-ranged density-coupled order, however, is crucial for the model, because it makes it realistic to assume an ultralocal Hamiltonian. In this way the model realizes the ultimate consequence of the lack of long-ranged order.

- **Fact 8:** The Debye-Stokes-Einstein relation is often violated in viscous liquids.

An important finding of the 1990’s was that translational motions often decouples from and becomes 1-3 decades faster than the rotations [32]. Somehow, translations are “enhanced” compared to what one expects from the Debye-Stokes-Einstein relation that estimates the single particle diffusion constant \( D_s \) from the viscosity \( \eta \). Although this relation \textit{a priori} applies only for macroscopic particles, there is no obvious reason that a molecule on average should move much longer than a during the rotational correlation time, the alpha relaxation time.

The generally accepted picture of Debye-Stokes-Einstein violations is that these reflect dynamic heterogeneity. This is not inconsistent with the model, because the model provides a coarse-grained description of the dynamics. Debye-Stokes-Einstein violations actually fit nicely with the model if one assumes that the single-particle diffusion constant is roughly equal to the diffusion constant \( D \) of Eq. (7); in this case the long-wavelength dominance inequality \( \bowtie \) simply expresses the Debye-Stokes-Einstein violation.

- **Fact 9:** The dynamics are independent of the chemistry.

At any given temperature the relaxation characteristics – linear as well as nonlinear – are similar for all liquids. Of course viscous liquids do differ as regards, e.g., whether or not there is a clearly defined beta relaxation in the liquid phase, and whether or not time-temperature superposition applies. But these differences do not appear to correlate with chemical differences in any simple fashion. For instance, as regards their dielectric and thermodynamics properties, liquids held together exclusively by van der Waals forces do not differ systematically from those involving hydrogen bonds. Measurements on viscous metallic liquids forming bulk metallic glasses show that their frequency-dependent shear modulus is indistinguishable from that of typical molecular liquids [33]. The overall conclusion is that from macroscopic measurements alone it is not possible to determine which kind of chemical bonds are involved (except of course from the temperature range where the glass transition takes place that trivially provides information about the strength of the intermolecular forces). As a further confirmation of fact 9 it should be noted that mixtures of different molecules behave much like pure liquids and that, again, it is not possible from purely macroscopic measurements to tell whether or not a given liquid is a mixture.

The independence of chemistry is a highly significant fact. For some reason the dynamics are indifferent to details of the molecular interactions, but why? In the model chemistry independence is a natural consequence of the long-wavelength dominance of the dynamics; clearly chemistry plays little role for dynamics on length scales much longer than the size of a molecule. The chemistry independence of the model is similar to that in critical phenomena. As mentioned, a related line of reasoning has motivated many attempts to draw parallels to the theory of critical phenomena by assuming that viscous slowing down is accompanied by some kind of long-ranged order responsible for the observed quasi-universality. The above model has no such assumption. On the contrary, the model assumes that there are only short-ranged static correlations of the relevant fields, allowing for the simplification inherent in an ultralocal field theory. Only when it comes to the \textit{dynamics} do long length scales play important roles.
V. DISCUSSION

It is a long-standing assumption that viscous-liquid dynamics are cooperative. Mode-coupling theory is an interesting case where cooperativity enters via the coupling of single-particle motion to the surroundings, resulting in a modification of the single-particle motion with drastic consequences at low temperatures (infinite relaxation time at a finite temperature in the simplest version of the theory). Obviously, all molecular motion in a liquid must be cooperative in some sense because, due to the close packing, when one molecule moves, neighboring molecules must move as well. This applies for highly viscous liquids just as for the “ordinary” liquids traditionally studied by theorists. The present model is also cooperative, but in a rather simple-minded sense. There are two elements of cooperativity: 1) Density nonconservative, but in a rather simple-minded sense. There are two elements of cooperativity: 1) Density nonconservation (that implies $\Gamma_0 \neq 0$) is a cooperative effect because it involves the solidity-based movement of molecules even far away from a flow event; 2) The long-wavelength assumption Eq. [8] expresses cooperativity in the sense that motion over long wavelengths is involved in the alpha relaxation process.

The purpose of this paper was to show that the model of Ref. [14] and paper IV has predictions that were not put into the model. The fact that the model is consistent with – and in some cases predicts – several experimental facts strengthens its overall credibility. To further develop the model one should evaluate the quantitative model predictions. These may be revealed by brute-force computer simulations, which will not run into the well-known problem of molecular dynamics that it is impossible to simulate a liquid with, e.g., an alpha relaxation time of 1 second. This is possible in the model, simply because the vibrational degrees of freedom are not included in the description. – Finally we would like to point out that, despite the macroscopic reasoning of this paper, the long-wavelength dominance inequality Eq. [8] relates directly to properties of the individual flow events [34].

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[17] By an unfortunate mistake, in Ref. [8] the “kinematic viscosity” of the Navier-Stokes equation (viscosity over density, a quantity with same dimension as a diffusion constant) was referred to as the “dynamic viscosity.” The kinematic viscosity is the transverse momentum diffusion constant, a quantity that becomes very large when a liquid approaches the calorimetric glass transition. This is responsible for the fact that momentum is exchanged between liquid and measuring equipment over the alpha time scale, thus implying irrelevance of momentum conservation for realistic descriptions of viscous liquid dynamics as it is observed in the laboratory.
[19] There is one interesting exception, namely the so-called $\alpha'$ process of mono-hydroxy-alcohols which is indeed Debye, a process which is separated from and much slower than the ordinary alpha process determining the calorimetric $T_g$, see e.g. L. M. Wang, S. Shahriari, and R. Richert, J. Phys. Chem. B 109, 23255 (2005).
[25] The assumption of an ultralocal Hamiltonian means that there is a direct connection to the macroscopic thermodynamics of the relaxing degrees of freedom (i.e., the non-vibrational contribution to the thermodynamics), because the Hamiltonian is nothing more than the free energy of the relaxing degrees of freedom expressed as function of temperature and density.

The noise term of Eq. 5 obeys \( \langle \xi_k(t)\xi_k^*(t') \rangle = 2\Gamma_k\delta(t-t') \). On a very short time scale flow events are uncorrelated and thus the inequality Eq. 5 translates directly into properties of single flow events: If one flow event changes the density by \( \delta\rho_k \), one finds from IV that \( \langle |\delta\rho_k|^2 \rangle = \langle b^2 \rangle /N \) for \( k \to 0 \) where \( b \) (compare Eq. 1) is defined by the radial displacement far from the flow event varying as \(-b/(4\pi\langle\rho\rangle)1/r^2\) (IV), whereas the term \( k^2 \) is \( k^2 \langle \Delta R^2 \rangle /(3N) \) where \( \Delta R \) is the total displacement of all atoms induced by the flow event. On the other hand, integrating the noise term over a short time shows that \( \langle |\delta\rho_k|^2 \rangle \propto \Gamma_0 + Dk^2 \). Comparing these two expressions shows that the inequality Eq. 5 is equivalent to \( \langle b^2 \rangle \ll \langle \Delta R^2 \rangle /a^2 \). This could be obeyed either if \( |b| \ll 1 \) or the total displacement of all atoms induced by one flow event is much larger than the intermolecular distance \( a \).