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Space-resolved stress correlations and viscoelastic moduli for polydisperse systems: two faces of the stress noise

Jörg Baschnagel, Alexander N. Semenov*
Institut Charles Sadron, CNRS - UPR 22, Université de Strasbourg,
23 rue du Loess, BP 84047, 67034 Strasbourg Cedex 2, France

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Abstract

We discuss several advances in the theory of space-resolved stress correlations and viscoelastic relaxation moduli for liquids and other amorphous systems. Our study focuses on three aspects: (i) For a given wavevector $\underline{q}$ the $\underline{q}$-dependent longitudinal (parallel to $\underline{q}$) and transverse (perpendicular to $\underline{q}$) viscoelastic moduli of a fluid relax to equilibrium values in the long time limit $t \to \infty$. We derive relations for the $\underline{q}$-dependent equilibrium moduli in terms of generalized structure factors, which are valid for systems with mass polydispersity. (ii) We revisit an earlier derivation of the relation between the $\underline{q}$-dependent tensors of viscoelastic relaxation moduli (E) and stress correlations (C), which employed the concept of the "stress noise", but was also hinged on consideration of non-stationary flows. The new derivation of the C-E relation presented here is based on a conceptually simple argument avoiding non-stationary processes. (iii) We discuss the relevance of the mass current field for the $\underline{q}$-dependent viscoelastic relaxation moduli and the general relations between these moduli and correlation functions of the stress noise.

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1 Introduction

Mechanical stress and related viscoelastic relaxation moduli are among the main rheological characteristics defining the flow properties of complex fluids, including polymer melts and solutions [1], molten metallic alloys, soft-matter systems and glass-forming (supercooled) liquids [2–7]. Such viscoelastic systems are typically heterogeneous (being amorphous in nature) and combine the properties of viscous liquids and elastic solids, leading to a flow behavior that is generally determined by the stress tensor field, $\sigma_{\alpha\beta}(\underline{r}, t)$, and the associated stress correlation functions resolved in time t and in spatial position $\underline{r}$ (here α, β are Cartesian coordinates). The stress correlation functions are related to generalized wavevector ($\underline{q}$) dependent material functions. Relevant examples for these material functions include the shear, $G(q, t)$, and longitudinal, $L(q, t)$, relaxation moduli [8] (where $q = |\underline{q}|$) which show a spectrum of relaxation times and correlation lengths characterizing amorphous systems and defining their micro- and nano-rheological properties [9].

Spatio-temporal stress correlations have therefore been the subject of various theoretical and simulation studies in the past decade, e.g., for polymer melts [10,11] amorphous solids [5,12–14] and glass-forming liquids [8,15–20]. We also investigated these correlations by two theoretical approaches: on the one hand, by a combination of the linear response theory, the fluctuation-dissipation theorem (FDT) and the concepts inspired by the fluctuating hydrodynamics (see refs. 21,22), and, on the other hand, by the Zwanzig–Mori (ZM) projection operator formalism [23] (in collaboration with the Soft Condensed Matter Theory group in Konstanz building on their earlier work [15–17]).

The present paper is based on the studies of refs. 21,22, and aims at extending the analysis in two directions:

(i) The generalized shear and longitudinal relaxation moduli, $G(q, t)$ and $L(q, t)$, are the basic rheological material functions that can be obtained as special components from an underlying tensor $E_{\alpha\beta\gamma\delta}(\underline{q}, t)$ (of rank 4 with $\alpha, \beta, \gamma, \delta$ being Cartesian coordinates) which reflects the $(\underline{q}, t)$-dependent viscoelasticity of the system [22,23]. We therefore refer to the $\underline{E}$-tensor as the "tensor of generalized relaxation moduli" and also as the "elasticity tensor" because the long-time limit $E_{\alpha\beta\gamma\delta}(\underline{q}, t \to \infty) \equiv E^{\mathrm{e}}_{\alpha\beta\gamma\delta}(\underline{q})$ characterizes the purely static response of the (equilibrium) system to a deformation. As demonstrated in ref. 22, $E^{\mathrm{e}}_{\alpha\beta\gamma\delta}(\underline{q})$ in fluid regime is determined by two basic moduli: $L_{\mathrm{e}}(q)$ defining the longitudinal stress response to a weak longitudinal deformation wave, and $M_{\mathrm{e}}(q)$ defining the transverse stress response to the same deformation. Here we derive relations for $L_{\mathrm{e}}(q)$ and $M_{\mathrm{e}}(q)$ in terms of static correlation functions of structural variables. These relations are akin to the expression for the static structure factor $S(q)$ (see refs. 25,26) and may be useful to determine $L_{\mathrm{e}}(q)$ and $M_{\mathrm{e}}(q)$ from simulations.

(ii) In the macroscopic limit (*i.e.* at $q = 0$) the relaxation moduli may be expressed in terms of time-dependent equilibrium correlation functions of stress fluctuations [27]. A well known example is the shear relaxation modulus, $G(t) = G(q = 0, t)$, which is given by the correlation function of shear stress fluctuations [25,26]. As it was shown in refs. 21–23, the relations between the

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relaxation moduli and the stress fluctuations can be generalized to the case of finite wavevectors, $\underline{q} \neq 0$. Some of such generalized relations, involving $G(q,t)$ and $L(q,t)$, are known for a long time (*cf.* ref. 28), while another one for the transverse modulus $M(q,t)$ ($\rightarrow M_\mathrm{e}(q)$ for $t \rightarrow \infty$) was first obtained in ref. 21. In ref. 22 we employed the FDT and the concept of "stress noise" [8,21,22] to derive a general tensorial relation between the elasticity tensor $E_{\alpha\beta\gamma\delta}(\underline{q},t)$ and the tensor $C_{\alpha\beta\gamma\delta}(\underline{q},t)$ of the time correlation function of stress fluctuations, $\sigma_{\alpha\beta}(\underline{q},t)$, at finite $\underline{q}$. The derivation of this C-E relation (*cf.* eqn (115) in ref. 22 and also eqn (51) below) was based on the idea that a "no-flow constraint" (at a given $\underline{q}$) first eliminates fluctuations of the mass current (momentum) density for $t < 0$, while these fluctuations are then restored when the constraint is released for $t \geq 0$. Although the no-flow constraint renders the phase-space trajectory of the system's microstate non-stationary, the resulting C-E relation involves only the stationary equilibrium (ensemble-averaged) time correlation functions. This dichotomy might obscure the general validity of the C-E relation, despite the fair arguments provided in ref. 22. Therefore, here we present a novel derivation of the C-E relation which does not resort to the no-flow constraint.

Our paper is organized as follows: As this work addresses several open issues from previous studies, [21,22] our presentation begins in section 2 with a summary of the basic dynamical variables, the general relations between them, and the main findings and concepts from ref. 21 and 22, which are required for understanding of the new results in the two sections that follow. First, section 3 considers the $\underline{q}$-dependent elastic moduli in the static regime, $t \rightarrow \infty$. We establish the general relations between these moduli and equilibrium structural correlation functions. Then, we present in section 4 a new derivation of the relation between the stress-correlation tensor $C_{\alpha\beta\gamma\delta}(\underline{q},t)$ and the elasticity tensor $E_{\alpha\beta\gamma\delta}(\underline{q},t)$. Our new derivation avoids application of either the no-flow constraint (either stationary or non-stationary) or the ZM projection operator formalism. It thereby confirms the general validity of the C-E relation, eqn (51). The discussion presented in sections 2 to 4 reveals the different faces of the stress noise: On the one hand, its auto-correlation function is directly related to the generalized elasticity tensor (see section 2.2). On the other hand, the stress noise serves as a driving force generating fluctuations of velocity, concentration, and eventually of the total stress (see section 4). Moreover, we have recently unhidden a third face of the stress noise, which turned out to be intimately related to the "reduced deviatoric stress" introduced in an approach to stress correlations based on the Zwanzig–Mori projection operator formalism (see refs. 23 and 24). A discussion and summary of the main results are provided in section 5.

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2 Basic equations and definitions of the fields encoding liquid dynamics

2.1 Density, velocity and stress fields, and the generalized relaxation moduli

Let us consider a liquid of $N \gg 1$ particles in volume V. A particle 'i' has mass m_i, position $\underline{r}_i$ and velocity $\underline{v}_i$. The mean particle mass, concentration and mass density, respectively, are:

$$\bar{m} = \frac{1}{N}\sum_{i=1}^{N} m_i, \quad c_0 = N/V, \;\; \rho_0 = \bar{m}c_0. \tag{1}$$

The mass density field is defined as

$$\rho(\underline{r}, t) = \sum_i m_i \delta(\underline{r} - \underline{r}_i(t)), \tag{2}$$

while the momentum density is

$$\underline{J}(\underline{r}, t) = \sum_i m_i \underline{v}_i(t) \delta(\underline{r} - \underline{r}_i(t)). \tag{3}$$

The two fields are related by the mass balance equation: [25,26]

$$\frac{\partial \rho(\underline{r}, t)}{\partial t} = -\frac{\partial}{\partial r_\alpha} J_\alpha(\underline{r}, t), \tag{4}$$

where summation over repeated indices α is assumed (α denotes a Cartesian coordinate).

Next, we define the concentration and velocity fields following ref. 22 where the contribution of each particle is weighted with the factor $m_i/\bar{m}$ proportional to the particle mass:

$$c(\underline{r}, t) = \sum_i (m_i/\bar{m})\, \delta(\underline{r} - \underline{r}_i(t)) = \rho(\underline{r}, t)/\bar{m}, \tag{5}$$

$$\underline{v}(\underline{r}, t) = \frac{1}{c_0} \sum_i (m_i/\bar{m})\, \underline{v}_i(t) \delta(\underline{r} - \underline{r}_i(t)) = \underline{J}(\underline{r}, t)/\rho_0. \tag{6}$$

Note that the thus defined $c(\underline{r}, t)$ and $\underline{v}(\underline{r}, t)$ are proportional to the mass density and the momentum density, respectively. While eqn (6) is known [29] and is also referred to as "barycentric (or center of mass) velocity" [30], eqn (5) may appear unusual. The main reason why the c and $\underline{v}$ fields are defined with mass factors, $m_i/\bar{m}$, is that with such definitions they are connected to each other and to the stress field [*cf.* eqn (12)] by the fundamental conservation laws (*cf.* eqn (4) above and eqn (11) below). Other reasons supporting the adopted definitions, eqn (5) and (6), are considered in section 5. Obviously, in monodisperse systems (with

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particles of equal mass) eqn (5) and (6) coincide with 'conventional' definitions of concentration and collective velocity fields. [25,26]

The spatial Fourier transforms of the c and $\underline{v}$ fields (indicated solely by the argument $\underline{q}$) are (*cf.* eqn (30) of ref. 22):

$$c(\underline{q},t) \equiv \frac{1}{V}\int c(\underline{r},t)\mathrm{e}^{-\mathrm{i}\underline{q}\cdot\underline{r}}\mathrm{d}^d r = \frac{1}{V}\sum_i (m_i/\bar{m})\exp[-\mathrm{i}\underline{q}\cdot\underline{r}_i(t)], \tag{7}$$

$$\underline{v}(\underline{q},t) = \frac{1}{N}\sum_i (m_i/\bar{m})\,\underline{v}_i(t)\exp[-\mathrm{i}\underline{q}\cdot\underline{r}_i(t)], \tag{8}$$

where $\underline{q}$ is the wavevector and d is the space dimension. The mass current density in Fourier space is

$$\underline{J}(\underline{q},t) = \frac{1}{V}\sum_i m_i\underline{v}_i(t)\exp[-\mathrm{i}\underline{q}\cdot\underline{r}_i(t)]. \tag{9}$$

Obviously, $\underline{J}(\underline{q},t) = \rho_0\underline{v}(\underline{q},t)$. Note that the first equation in eqn (7) is the definition of the Fourier transform adopted in the present paper. It ensures that physical dimensions of transformed and original functions are the same.

The mass conservation law [*cf.* eqn (4)] in terms of the concentration [eqn (7)] and velocity [eqn (8)] fields becomes

$$\frac{1}{c_0}\frac{\partial c(\underline{q},t)}{\partial t} = -\mathrm{i}\underline{q}\cdot\underline{v}(\underline{q},t). \tag{10}$$

Furthermore, the fundamental momentum balance equation defines the rate of change of momentum density $\underline{J}(\underline{r},t)$:

$$\frac{\partial J_\alpha(\underline{r},t)}{\partial t} = \frac{\partial}{\partial r_\beta}\sigma_{\alpha\beta}(\underline{r},t). \tag{11}$$

Here $\sigma_{\alpha\beta}(\underline{r},t)$ is the stress tensor field, whose microscopic definition is [31,32]

$$\sigma_{\alpha\beta}(\underline{r},t) = \sum_{i>j} F_{ij\alpha}r_{ij\beta}\int_0^1 \delta\left(\underline{r}-\underline{r}_i+s\underline{r}_{ij}\right)\mathrm{d}s - \sum_i m_i v_{i\alpha}v_{i\beta}\delta\left(\underline{r}-\underline{r}_i\right), \tag{12}$$

where $v_{i\alpha}$ is component α of the velocity of particle i, δ is the d-dimensional delta-function, $r_{ij\beta}$ is β-component of vector $\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$, and $F_{ij\alpha}$ is the α-component of the force acting on particle i from particle j (all vectors here are taken at time t). The force is given by $F_{ij\alpha} \equiv (\frac{r_\alpha}{r}u'_{ij}(r))_{\underline{r}=\underline{r}_j-\underline{r}_i}$ with $u_{ij}(r)$ being the pairwise interaction energy of particles i and j, and $u'_{ij}(r) \equiv \frac{\mathrm{d}u_{ij}(r)}{\mathrm{d}r}$. The Fourier transform of eqn (12) yields the wavevector dependent stress (*cf.* ref. 22, 23 and 26):

$$\begin{aligned}\sigma_{\alpha\beta}(\underline{q},t) &\equiv \frac{1}{V}\int \sigma_{\alpha\beta}(\underline{r},t)\mathrm{e}^{-\mathrm{i}\underline{q}\cdot\underline{r}}\,\mathrm{d}^d r \\ &= \frac{1}{V}\sum_{i>j}\frac{F_{ij\alpha}r_{ij\beta}}{\mathrm{i}\underline{q}\cdot\underline{r}_{ij}}\left(\mathrm{e}^{-\mathrm{i}\underline{q}\cdot\underline{r}_i} - \mathrm{e}^{-\mathrm{i}\underline{q}\cdot\underline{r}_j}\right) - \frac{1}{V}\sum_i m_i v_{i\alpha}v_{i\beta}\mathrm{e}^{-\mathrm{i}\underline{q}\cdot\underline{r}_i},\end{aligned} \tag{13}$$

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which appears in the momentum equation in the wavevector representation [upon Fourier transformation of eqn (11)],

$$\rho_0 \frac{\partial v_\alpha(\underline{q},t)}{\partial t} = \mathrm{i} q_\beta \sigma_{\alpha\beta}(\underline{q},t), \tag{14}$$

where $v_\alpha(\underline{q},t)$ is the α-component of the $\underline{q}$-dependent velocity field [*cf.* eqn (8)]. Note that here and in what follows we always assume $\underline{q} \neq 0$.

After introducing the essential dynamic variables and the fundamental balance laws we are now in a position to define the tensor of generalized ($\underline{q}$-dependent) relaxation moduli (or elasticity tensor) $E_{\alpha\beta\gamma\delta}(\underline{q},t)$. Let us consider an amorphous (liquid or solid) system in a given microstate Γ at $t = 0^-$. At $t = 0$ the system is then slightly deformed, either by a perturbative external force field [1] or by application of an infinitesimal displacement, $\underline{u}(\underline{r}) = \underline{u}(\underline{q})\mathrm{e}^{\mathrm{i}\underline{q}\cdot\underline{r}}$, to each particle, when a particle located at position $\underline{r}$ is instantly shifted from $\underline{r}$ to $\underline{r} + \underline{u}(\underline{r})$. This leads to the strain field

$$\gamma_{\alpha\beta}(\underline{r}) = \frac{\partial u_\alpha(\underline{r})}{\partial r_\beta} \tag{15}$$

at $t = 0^+$. [2] The strain generates a force variation, $\partial\sigma_{\alpha\beta}(\underline{r},t)/\partial r_\beta$, which in turn entails a change of the velocity field, leading to additional strains and so on. For $t > 0$ a flow is therefore induced by the initial perturbation. The deformation associated with this flow can be characterized by the strain rate $\dot\gamma_{\alpha\beta}(\underline{r},t)$ defined as $\dot\gamma_{\alpha\beta}(\underline{r},t) \equiv \frac{\partial\gamma_{\alpha\beta}(\underline{r},t)}{\partial t} = \frac{\partial v_\alpha(\underline{r},t)}{\partial r_\beta}$ or, upon Fourier transformation, as [*cf.* eqn (8)]

$$\dot\gamma_{\alpha\beta}(\underline{q},t) \equiv \mathrm{i} q_\beta v_\alpha(\underline{q},t). \tag{16}$$

Let us now consider an equilibrium ensemble of systems with canonical distribution in the Hamiltonian phase space of all possible microstates Γ to which the above deformation is applied at $t = 0$. Since this instantaneous deformation is infinitesimal, the response of the stress tensor—*i.e.* the ensemble-averaged increment of the stress tensor, $\langle\delta\sigma_{\alpha\beta}(\underline{q},t)\rangle$, due to the perturbation—is related to the ensemble-averaged strain, $\langle\dot\gamma_{\alpha\beta}(\underline{q},t)\rangle\,\mathrm{d}t$, [3] in a linear fashion (cf refs. 22,25). Taking into account the uniformity in space and time of the equilibrium amorphous system (at the ensemble-averaged level), the general form of this linear response relation is (*cf.* eqn (33) in ref 22)

$$\langle\delta\sigma_{\alpha\beta}(\underline{q},t)\rangle = \int_{0^-}^{t} E_{\alpha\beta\gamma\delta}(\underline{q},t-t')\,\langle\dot\gamma_{\gamma\delta}(\underline{q},t')\rangle\,\mathrm{d}t'. \tag{17}$$

Here the kernel $E_{\alpha\beta\gamma\delta}(\underline{q},t)$ reflects the susceptibility of the system to an infinitesimal $(\underline{q},t')$-dependent strain $\langle\dot\gamma_{\alpha\beta}(\underline{q},t')\rangle\,\mathrm{d}t'$ by describing how much stress remains

[1] See section 5.1 in ref. 22 and also eqn (75) in the Discussion and Summary section.

[2] Along with the affine shift of positions, the momenta of the particles must also be changed appropriately to render the whole transformation canonical (see section 2 in ref. 21 and section 5.1 of ref. 22).

[3] Here $\langle\ldots\rangle$ means an ensemble average over all microstates Γ according to the (canonical) equilibrium distribution in the phase space at $t = 0^-$.

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at time $t-t'$ from the strain at time t' and selected wavevector $\underline{q}$. Therefore, the E-tensor is a material function characterizing the spatially and temporally resolved viscoelastic response of the equilibrium system at the ensemble-averaged level. Eqn (17) invokes the Boltzmann superposition principle [1] by summing all stress increments, $E_{\alpha\beta\gamma\delta}(\underline{q}, t-t')\left\langle\dot{\gamma}_{\gamma\delta}(\underline{q}, t')\right\rangle \mathrm{d}t'$, from the time when the deformation was imposed ($t = 0^-$) up to time t. The upper limit (t) comes from the causality principle dictating that

$$E_{\alpha\beta\gamma\delta}\left(\underline{q}, t < 0\right) \equiv 0. \tag{18}$$

Since the E-tensor is a characteristic property of the material, it does not depend on the particular way the deformation is imposed: whether it is due to particle displacements or due to an external force field, as was proved elsewhere (*cf.* section 5.1 of ref 22 for more details). We will return to the latter point in the Discussion and Summary section.

In the limit $q \to 0$, the E-tensor is related to the generalized time-dependent viscosity tensor studied in rheology. [22]. On the other hand, in the static limit, *i.e.* for $t \to \infty$, the E-tensor tends to the "equilibrium elasticity tensor", [22,23]

$$E_{\alpha\beta\gamma\delta}(\underline{q}, t \to \infty) \equiv E^{\mathrm{e}}_{\alpha\beta\gamma\delta}(\underline{q}), \tag{19}$$

which characterizes the elastic properties of the equilibrium system. Therefore, we also refer to the E-tensor as the elasticity tensor in what follows. Note that $t \to \infty$ in eqn (19) is considered as a very long (perhaps inaccessible in practice) time sufficient for a complete equilibration of the system.

2.2 Stress correlation functions, deterministic stress and stress noise

In section 4 we will consider the relation between the elasticity tensor $E_{\alpha\beta\gamma\delta}(\underline{q}, t)$ and the stress correlation function $C_{\alpha\beta\gamma\delta}(\underline{q}, t)$. This stress correlation function is defined as [21,22]

$$C_{\alpha\beta\gamma\delta}(\underline{q}, t) \equiv \frac{V}{T}\left\langle\sigma_{\alpha\beta}(\underline{q}, t+t')\sigma_{\gamma\delta}(-\underline{q}, t')\right\rangle, \quad q \neq 0 \tag{20}$$

(*cf.* eqn (72) in ref 22 and eqn (6) in ref 21). Here T is temperature in energy units (*i.e.* Boltzmann constant $k_{\mathrm{B}} \equiv 1$) and angular brackets, $\langle ...\rangle$, mean both ensemble averaging over all microstates Γ and gliding averaging with respect to t'. Eqn (20) applies to equilibrated systems, hence $\left\langle\sigma_{\alpha\beta}(\underline{q}, t)\right\rangle = 0$ for $q \neq 0$. Therefore, the instantaneous stress tensor, $\sigma_{\alpha\beta}(\underline{q}, t)$, itself represents the stress fluctuation if $q \neq 0$. The correlation function defined in eqn (20) is real and shows both minor ($\alpha\beta \leftrightarrow \beta\alpha$) and major symmetries ($\alpha\beta \leftrightarrow \gamma\delta$) [21,23]

$$C_{\alpha\beta\gamma\delta}(\underline{q}, t) = C_{\beta\alpha\gamma\delta}(\underline{q}, t) = C_{\gamma\delta\alpha\beta}(\underline{q}, t). \tag{21}$$

Note that $C_{\alpha\beta\gamma\delta}(\underline{q}, t)$ depends on the wavevector $\underline{q}$, and not only on its norm q, for the equilibrium amorphous systems considered (which exhibit, on ensemble

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averaging, translational and rotational invariances, the time-reversal symmetry and achirality). [12–14,16,22,33]

Following ref 21 and 22 we decompose the total stress, $\sigma_{\alpha\beta}(\underline{q},t)$, into two contributions: the "deterministic stress" $\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t)$ and the "stress noise" $\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},t)$,

$$\sigma_{\alpha\beta}(\underline{q},t) = \sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t) + \sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},t). \tag{22}$$

The deterministic stress of the time-dependent microstate $\Gamma(t)$ is defined by its deformation (flow) history as

$$\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t) = \int_{-\infty}^{t} E_{\alpha\beta\gamma\delta}\left(\underline{q},t-t'\right) \mathrm{i} v_{\gamma}\left(\underline{q},t'\right) q_{\delta} \mathrm{d}t'. \tag{23}$$

Here $v_{\gamma}(\underline{q},t')$ is the γ-component of the Fourier transform of the instantaneous velocity field defined in eqn (8), while $E_{\alpha\beta\gamma\delta}(\underline{q},t-t')$ is the same elasticity tensor as defined in eqn (17): it characterizes the spatio-temporal viscoelasticity of the system at the ensemble-averaged level.

The definition of $\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t)$ in eqn (23) is formally similar to eqn (17) for $\langle\delta\sigma_{\alpha\beta}(\underline{q},t)\rangle$. However, these two equations are conceptually different due to their physical interpretation. In eqn (17) $\langle\delta\sigma_{\alpha\beta}(\underline{q},t)\rangle$ is the ensemble-averaged stress response resulting from the ensemble-averaged strain rate $\langle\dot{\gamma}_{\gamma\delta}(\underline{q},t')\rangle = \mathrm{i}\langle v_{\gamma}\left(\underline{q},t'\right)\rangle q_{\delta}$ that was triggered by a perturbation of each microstate in the ensemble at $t_0 = 0^-$. Before the perturbation was applied (*i.e.* for $t' < 0$), the system was at equilibrium, with no flow on average $\langle v_{\gamma}\left(\underline{q},t'<0\right)\rangle = 0$, and that is why the lower bound of the integral in eqn (17) is set to $t_0 = 0^-$. By contrast, both $\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t)$ and $v_{\gamma}\left(\underline{q},t'\right)$ in eqn (23) characterize an individual trajectory in the phase space (*i.e.* for a microstate from the equilibrium ensemble). In this case, there is no external perturbation, which is accounted for by taking $t_0 = -\infty$ as the lower bound of the integral in eqn (23). [4]

According to its definition, eqn (23), $\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t)$ is the part of the total stress that is directly related to the microscopic dynamics of the velocity field, $v_{\gamma}(\underline{q},t')$, for all times $t' \leq t$. Since no coarse-graining in either space or time is applied, $\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t)$ reflects all fluctuations of the flow, $v_{\gamma}(\underline{q},t')$, including those of high frequency.

The stress noise, $\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},t)$, is formally defined by eqn (22) as the difference between the total and the deterministic stress, $\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},t) = \sigma_{\alpha\beta}(\underline{q},t) - \sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t)$: It therefore represents the complementary part of the total stress, which is decoupled from the flow at the selected wavevector $\underline{q}$, and is caused by the structural, compositional, enthalpic and other thermal fluctuations unrelated to the deformation in the system. [21,22] The correlation function of stress noise can be defined in analogy with eqn (20):

$$C^{\mathrm{n}}_{\alpha\beta\gamma\delta}(\underline{q},t) \equiv \frac{V}{T}\left\langle \sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},t+t')\sigma^{\mathrm{n}}_{\gamma\delta}(-\underline{q},t')\right\rangle. \tag{24}$$

[4]Note that in order to avoid a fictitious divergence of the integral in eqn (23), a factor $\mathrm{e}^{\epsilon t}$ should be introduced in the integrand and the limit $\epsilon \to 0$ should be taken as the last step (see *e.g.* ref. 25, p. 231). For clarity of presentation we omit this factor here.

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At long times, $C^{\rm n}_{\alpha\beta\gamma\delta}(\underline{q},t)$ must vanish since $\langle\sigma^{\rm n}_{\alpha\beta}(\underline{q},t')\rangle = 0$ and the terminal relaxation time is finite: $C^{\rm n}_{\alpha\beta\gamma\delta}(\underline{q},t) \to 0$ at $t \to \infty$.

It was recently shown [22,23] that the correlation function of the stress noise ($C^{\rm n}$) is closely related to the elasticity tensor (E):

$$C^{\rm n}_{\alpha\beta\gamma\delta}(\underline{q},t) = E_{\alpha\beta\gamma\delta}(\underline{q},|t|) - E^{\rm e}_{\alpha\beta\gamma\delta}(\underline{q}), \qquad (25)$$

where $|t|$ in the rhs is required since $C^{\rm n}$ is even in time, while the convention $E = 0$ at $t < 0$ is adopted due to causality [*cf.* eqn (18)].

Eqn (25) is remarkable in two respects: First, it connects the correlation function of the fluctuating stress noise with dissipative viscoelastic effects encoded in the E-tensor. This is reminiscent of the relation between the friction coefficient of a Brownian particle (dissipative term) and the correlation function of the random force (noise term) in the Langevin equation [34,35] and, beyond that, also of the classical Einstein relation connecting the mobility (inverse friction coefficient) of a tracer particle in a liquid—which defines the particle's drift velocity in response to a driving force—with tracer's self-diffusion constant D reflecting the Brownian motion in the system (see ref. 36). Noteworthily, the Einstein relation was generalized in order to predict the mean-square displacement (MSD) of the center-of-mass of a polymer chain in a melt, leading to a non-trivial time dependence of the MSD. [11,37–40]

Second, eqn (25) indicates a method to determine all components ($\alpha\beta\gamma\delta$) of the E-tensor from stress fluctuations. Having the E-tensor at hand would provide a complete description of the spatio-temporal viscoelasticity of the amorphous system. To apply eqn (25) one has to know the static q-dependent elastic moduli, $E^{\rm e}_{\alpha\beta\gamma\delta}(\underline{q})$. We address this problem in section 3 where we present a new approach to calculating $E^{\rm e}_{\alpha\beta\gamma\delta}(\underline{q})$ from simulations.

3 Equilibrium elastic moduli of a liquid or amorphous solid

3.1 Generalized compressibility equation (GCE)

A deformation (flow) of an amorphous system generates a stress response defined by three main $\underline{q}$-dependent relaxation moduli: [21,22] the shear modulus, $G(q,t) = E_{2121}(q,t)$, the longitudinal modulus, $L(q,t) = E_{1111}(q,t)$, and the mixed (transverse) modulus, $M(q,t) = E_{2211}(q,t)$. Here the Cartesian components correspond to the naturally rotated coordinates (NRC) with axis 1 parallel to the wavevector $\underline{q}$ and axis 2 perpendicular to it. [33]

The *static* response in liquids is given by the long-time limit ($t \to \infty$) of these relaxation moduli: [21–23]

$$G_{\rm e}(q) \equiv G(q,t\to\infty) = 0,\ \ L_{\rm e}(q) \equiv L(q,t\to\infty),\ \ M_{\rm e}(q) \equiv M(q,t\to\infty). \qquad (26)$$

In amorphous glassy systems a complete relaxation is impossible as the terminal relaxation time in such systems is not accessible experimentally. So, one has

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to distinguish between the long-time elastic moduli, $G_{\rm pl}(q) > 0$, $L_{\rm pl}(q)$, and $M_{\rm pl}(q)$, corresponding to the glassy plateau on intermediate, though long, time scales, and the genuine static moduli, $G_{\rm e}(q) = 0$, $L_{\rm e}(q) > 0$ and $M_{\rm e}(q) > 0$, characterizing the stress response upon complete relaxation of an amorphous system. [5] That is why we prefer to call $L_{\rm e}$ and $M_{\rm e}$ the equilibrium elastic moduli in order to distinguish them from the glassy plateaux [6] occurring in supercooled liquids at intermediate time-scales which strongly increase on cooling towards the glass transition temperature $T_{\rm g}$. Obviously, the static and equilibrium moduli are the same in the high-temperature liquid regime.

It is widely accepted that the equilibrium longitudinal modulus $L_{\rm e}(q)$ is related to the collective static structure factor $S(q)$,

$$S(q) = \frac{1}{N}\sum_{i,j=1}^{N} \left\langle \exp\left(\mathrm{i}\underline{q}\cdot\left(\underline{r}_i - \underline{r}_j\right)\right)\right\rangle , \tag{27}$$

via the generalized compressibility equation (GCE) [22,23,25,26,41]

$$L_{\rm e}(q) = c_0 T/S(q), \quad q \neq 0. \tag{28}$$

For monodisperse systems eqn (28) reduces to the classical compressibility equation in the limit $q \to 0$: [25,26,42]

$$\kappa_T = S(q \to 0)/\left(c_0 T\right), \tag{29}$$

where

$$\kappa_T = -\left(\frac{\partial P}{\partial \ln V}\right)_T^{-1} = \frac{1}{L_{\rm e}^{\rm bulk}} \tag{30}$$

is the static isothermal compressibility of the system and P is the (mean) pressure. Thus, the longitudinal elastic modulus $L_{\rm e}(q \to 0)$ coincides with the bulk compression modulus $L_{\rm e}^{\rm bulk}$ of a monodisperse liquid. [43] However, the latter statement and eqn (29) are not valid for polydisperse systems where, in addition to compressibility effects, composition fluctuations also need to be taken into account, as discussed *e.g.* in refs 8, 25 and 43.

Moreover, while the GCE, eqn (28), is valid for systems with particles of equal mass, it is not applicable as such to systems composed of particles with polydisperse masses. A derivation of a more general equation, valid also for systems with mass polydispersity, is presented in Appendix B. The result can also be understood in simpler terms, as outlined in the next section.

3.2 GCE for polydisperse systems

Let us consider a liquid at or near equilibrium. The free energy $\mathcal{F}$ associated with a collective fluctuation of a given amplitude a—like a concentration wave at wavevector $\underline{q}$, [7] for which $a = c(\underline{q})$, *cf.* eqn (7)—is proportional to the total

[5] Complete relaxation for deeply supercooled liquids, even below the (extrapolated) glass transition temperature, can be achieved in computer simulations of model systems by applying particle swaps in polydisperse systems of Lennard-Jones particles. [44–46]

[6] Often, the plateau values are also referred to as 'non-ergodicity parameters'. [7,47,48]

[7] By concentration we mean the reduced density as defined in eqn (5) and (7).

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volume V of the system (more precisely, to $V\,|a|^2$). Therefore, the typical amplitude a must be small for large systems, given that the typical free energy of a thermal fluctuation must be comparable with the thermal energy T. This implies that $\mathcal{F}$ can be well approximated by a quadratic form, $\mathcal{F} \simeq \frac{\kappa V}{2}\,|a|^2$, where κ depends on q, $\kappa = \kappa(q)$. This also means that the fluctuation statistics are Gaussian, leading to $\langle |a|^2 \rangle = T/(\kappa V)$. [8] Thus, for $a = c(\underline{q})$ we get

$$\left\langle \left| c(\underline{q}) \right|^2 \right\rangle = T/(\kappa V). \tag{31}$$

Defining the generalized structure factor $S_2(q)$ as (see also ref. 49 and references therein)

$$S_2(q) = \frac{1}{N} \sum_{i,j=1}^{N} \left(m_i m_j / \bar{m}^2 \right) \left\langle \exp\left(\mathrm{i}\underline{q} \cdot \left(\underline{r}_i - \underline{r}_j \right) \right) \right\rangle, \tag{32}$$

we find from eqn (104) in Appendix B

$$\kappa(q) = \frac{T}{c_0 S_2(q)}. \tag{33}$$

Let us now take into account that an increment of the concentration wave amplitude, $\delta c(\underline{q})$, must be proportional to the longitudinal deformation $\delta\gamma$, as follows from eqn (10) and (16): [9]

$$\delta c(\underline{q})/c_0 = -\delta\gamma(\underline{q}), \tag{34}$$

and that the free energy increment, $\delta\mathcal{F}$, associated with an infinitesimal strain $\delta\gamma$ is proportional to the longitudinal stress $\sigma_{11}(\underline{q})$: [25]

$$\delta\mathcal{F} = V\sigma_{11}(\underline{q})\delta\gamma(\underline{q})^*, \tag{35}$$

where NRC are used again. Recalling also that $\delta\mathcal{F} = V\kappa(q)c(\underline{q})\delta c(\underline{q})^*$, as follows from $\mathcal{F} \simeq \frac{\kappa V}{2}|c(\underline{q})|^2$, and using eqn (34) and (35), we find $\sigma_{11}(\underline{q}) = -\kappa(q)c_0 c(\underline{q})$. An increment of the longitudinal stress due to an increment of $c(\underline{q})$ therefore is $\delta\sigma_{11}(\underline{q}) = -\kappa(q)c_0\delta c(\underline{q})$, which gives on using again eqn (34):

$$\delta\sigma_{11}(\underline{q}) = \kappa(q)c_0^2\delta\gamma(\underline{q}). \tag{36}$$

By definition (*cf.* eqn (17), see also eqn (89) in Appendix B) the prefactor before $\delta\gamma$ in the above equation must be equal to the genuinely static longitudinal modulus $L_\mathrm{e}(q)$, hence

$$L_\mathrm{e}(q) = \kappa(q)c_0^2 = \frac{c_0 T}{S_2(q)}, \tag{37}$$

in agreement with eqn (105) of the Appendix B. Note that eqn (37) generalizes the classical compressibility equation (*cf.* eqn (28)) to systems with mass polydispersity for which the function $S_2(q)$ is different from the classical structure factor $S(q)$ (*cp.* eqn (27) and (32)).

[8] Here we take into account that a is a complex number with two components (its real and imaginary parts) involved in two fluctuation waves (with wavevectors $\underline{q}$ and $-\underline{q}$) whose total free energy is $2\mathcal{F}$.

[9] For simplicity we assume here that both $c(\underline{q})$ and $\delta c(\underline{q})$ are real.

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3.3 Cross-correlations between the longitudinal stress and concentration fluctuations

In Appendix B the GCE for systems with mass polydispersity, eqn (105), was derived based on a result for the cross-correlations between the longitudinal stress and concentration fluctuations [eqn (100)]. In this section, we provide an alternative derivation of eqn (100) which will be useful for the discussion on the transverse modulus $M_\mathrm{e}(q)$ in section 3.4.

Let us begin by recalling the microscopic definition of the $\underline{q}$-dependent stress valid for a system of spherical particles with pairwise interactions (*cf.* ref 26 and eqn (70) of ref. 22 or eqn (13) of ref. 23):

$$\sigma_{\alpha\beta}(\underline{q}) = \sigma^{\mathrm{vir}}_{\alpha\beta}(\underline{q}) + \sigma^{\mathrm{id}}_{\alpha\beta}(\underline{q}), \tag{38}$$

where $\sigma^{\mathrm{id}}_{\alpha\beta}(\underline{q})$ is the ideal-gas stress due to particle momenta (*cf.* the last term in eqn (13)), and $\sigma^{\mathrm{vir}}_{\alpha\beta}(\underline{q})$ is the virial part of the stress due to pairwise interactions of the particles (*cf.* the first term in eqn (13)):

$$\sigma^{\mathrm{vir}}_{\alpha\beta}(\underline{q}) = \frac{1}{V}\sum_{i\neq j} u'_{ij}(r)\frac{r_\alpha r_\beta}{\mathrm{i}\underline{q}\cdot\underline{r}}\frac{1}{r}\mathrm{e}^{-\mathrm{i}\underline{q}\cdot\underline{r}_i}, \tag{39}$$

where the sum involves all ij pairs (with $i \neq j$) and $\underline{r} = \underline{r}_j - \underline{r}_i$. Note that eqn (38) and (39) are in agreement with eqn (13).

For the longitudinal stress component (with $\alpha = \beta = 1$; note that we use the NRC so that the axis 1 is parallel to the wavevector $\underline{q}$) eqn (39) can be simplified as

$$\sigma^{\mathrm{vir}}_{11}(\underline{q}) = \frac{1}{\mathrm{i}qV}\sum_{i\neq j} u'_{ij}(r)\frac{x}{r}\mathrm{e}^{-\mathrm{i}\underline{q}\cdot\underline{r}_i} = \frac{1}{\mathrm{i}qV}\sum_i f_{xi}\mathrm{e}^{-\mathrm{i}qx_i}, \tag{40}$$

where $x = \underline{r}\cdot\underline{q}/q$ is the coordinate along axis 1, and f_{xi} is the longitudinal projection (onto the x-axis) of the total force acting on particle i from all other particles:

$$f_{xi} = -\frac{\partial U(\Gamma)}{\partial x_i}. \tag{41}$$

Here $U(\Gamma)$ is the total interaction energy of all particles and Γ denotes the set of all their coordinates. Taking into account that the equilibrium system is macroscopically uniform which implies that a translation of each particle by a vector $\underline{u}_{\mathrm{tr}}$ conserves the total interaction energy and leads statistically to the same ensemble, we find from eqn (40) the cross-correlation function of the virial stress with concentration [*cf.* eqn (7)]:

$$\left\langle\sigma^{\mathrm{vir}}_{11}(\underline{q})c^*(\underline{q})\right\rangle = \frac{T}{V^2}\sum_{i\neq j}\frac{m_j}{\bar{m}}\left\langle\mathrm{e}^{\mathrm{i}q(x_j-x_i)}\right\rangle = \frac{Tc_0}{V}\left[S_1(q)-1\right], \tag{42}$$

where we used $\frac{\partial U(\Gamma)}{\partial x_i}\exp\left(-U(\Gamma)/T\right) = -T\frac{\partial}{\partial x_i}\exp\left(-U(\Gamma)/T\right)$, integration by parts, and the fact that the integrated term does not contribute due to periodic

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boundary conditions. The first term in square brackets in the very rhs of eqn (42) comes from the sum over all ij pairs, while the second term there corresponds to the 'diagonal' sum, $\sum_{i=j}$, which should be taken out. Here the function $S_1(q)$ is the modified structure factor defined as (*cf.* eqn (27) and (32))

$$S_1(q) = \frac{1}{N}\sum_{i,j=1}^{N}\frac{m_j}{\bar{m}}\left\langle \mathrm{e}^{\mathrm{i}q(x_j-x_i)}\right\rangle. \tag{43}$$

Turning now to the ideal-gas stress, we find:

$$\left\langle \sigma_{11}^{\mathrm{id}}(\underline{q})c^*(\underline{q})\right\rangle = -\frac{Tc_0}{V}S_1(q), \tag{44}$$

if we recall that $\sigma_{11}^{\mathrm{id}}(\underline{q})$ is defined by the last term in eqn (13) and that $\langle v_{i1}^2\rangle = T/m_i$ (where v_{i1} is the first component of velocity of particle i). Summing both sides of eqn (42) and (44) we arrive at

$$\left\langle \sigma_{11}(\underline{q})c^*(\underline{q})\right\rangle = -c_0T/V, \tag{45}$$

which coincides with eqn (100) in Appendix B.

3.4 Relation between the equilibrium transverse modulus and the structure factors

In order to obtain the transverse equilibrium modulus $M_{\mathrm{e}}(q)$ we need to calculate the cross-correlation function of the lateral stress, $\sigma_{22}(\underline{q})$, and concentration, $\left\langle \sigma_{22}(\underline{q})c^*(\underline{q})\right\rangle$. The stress-concentration correlation function can be decomposed into two parts, the virial, $\left\langle \sigma_{22}^{\mathrm{vir}}(\underline{q})c^*(\underline{q})\right\rangle$, and the ideal, $\left\langle \sigma_{22}^{\mathrm{id}}(\underline{q})c^*(\underline{q})\right\rangle$. The latter part is easily obtained, since the pre-averaging of $\sigma_{22}^{\mathrm{id}}(\underline{q})$ over the velocities gives exactly the same result as for the longitudinal stress component, leading to (*cf.* eqn (44))

$$\left\langle \sigma_{22}^{\mathrm{id}}(\underline{q})c^*(\underline{q})\right\rangle = -\frac{Tc_0}{V}S_1(q). \tag{46}$$

Turning to the virial part, the correlation function,

$$C_{\mathrm{vir}}(q) \equiv \left\langle \sigma_{22}^{\mathrm{vir}}(\underline{q})c^*(\underline{q})\right\rangle, \tag{47}$$

does not seem to be related to a conventional structure factor and, therefore, should be obtained by computer simulations in analogy with the procedure employed to get the standard structure factor $S(q)$. Here the numerical simulation task is expected to be somewhat more time-consuming, since for any particle i one has to take into account the contributions of all neighbors interacting with the particle. It may be convenient to define a function related to the correlation function $C_{\mathrm{vir}}(q)$ in analogy with eqn (44) as

$$\tilde{S}(q) = -\frac{V}{Tc_0}C_{\mathrm{vir}}(q). \tag{48}$$

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The function $\tilde{S}(q)$ will be referred to as the lateral structure factor. Note that this function is independent of V in the thermodynamic limit, just like the standard structure factor $S(q)$. The 'minus' sign in eqn (48) serves to render $\tilde{S}(q)$ positive since (at least at low q) the longitudinal and lateral stress components should be close to each other, and both stresses should anticorrelate with concentration (as a higher concentration in liquids must result in a higher pressure, hence lower stress). Combining eqn (46) and (48) we get

$$\left\langle \sigma_{22}(\underline{q})c^*(\underline{q})\right\rangle = -\frac{Tc_0}{V}\left[S_1(q)+\tilde{S}(q)\right]. \tag{49}$$

Finally, using the argument presented at the end of Appendix B below eqn (100), we find that the correlator $\langle AB^*\rangle$ (with $A=\sigma_{22}(\underline{q})$ and $B=c(\underline{q})$, see eqn (102) and (104)) is given by the rhs of eqn (49). Taking also into account that $\lambda = -M_{\rm e}(q)/c_0$ (instead of eqn (103)) we thus obtain

$$M_{\rm e}(q) = c_0 T\frac{S_1(q)+\tilde{S}(q)}{S_2(q)} = L_{\rm e}(q)\left[S_1(q)+\tilde{S}(q)\right], \tag{50}$$

where eqn (37) was used in the last step. This shows that $M_{\rm e}(q)$ and $L_{\rm e}(q)$ generally exhibit different dependence on q and other parameters, except at $q\to 0$ where $M_{\rm e}(q)-L_{\rm e}(q)\to 0$, implying that $S_1(q)+\tilde{S}(q)\to 1$ (*cf.* section 6.4 in ref. 22). Furthermore, note that $M_{\rm e}(q) = L_{\rm e}(q)+\mathcal{O}(q^2)$ at small q, as follows from $G_{\rm e}(q)=0$ and eqn (121) in ref. 22.

3.5 Discussion on equilibrium moduli

In the above sections we demonstrated that the genuinely static (equilibrium) q-dependent elastic moduli (corresponding to infinite time shift t), namely the longitudinal and transverse moduli, $L_{\rm e}(q) = L(q, t\to\infty)$ and $M_{\rm e}(q) = M(q, t\to\infty)$, can be related to stress-concentration cross-correlation functions at zero time shift (reflecting *structural* cross-correlations). More precisely, we found that $L_{\rm e}(q)$ can be obtained in the general case based on the static structure factor $S_2(q)$ defined in eqn (32) (*cf.* eqn (37)), while $M_{\rm e}(q)$ can be expressed in terms of three correlation functions, the structure factors $S_1(q)$ and $S_2(q)$ (*cf.* eqn (43) and (32)), and the lateral structure factor $\tilde{S}(q)$ related to cross-correlations of the transverse stress and concentration (*cf.* eqn (48)).

Thus, we established a link between the long-time moduli and structural correlations of concentration (reduced density) and stress. Importantly, this link provides an independent alternative way to calculate q-dependent equilibrium moduli, $L_{\rm e}(q)$ and $M_{\rm e}(q)$. Calculation of q-dependent relaxation moduli (like $L(q,t)$ and $M(q,t)$) proved to be a formidable problem. [8,20,50] This problem gets simpler in the limit of vanishing q, $q\to 0$, where $L_{\rm e}(q)$ and $M_{\rm e}(q)$ become equal. [22,27] However, even in the limiting case, $q\to 0$, calculation of the moduli in the long-time regime is a difficult task, since (i) very long simulation runs are needed, and (ii) the statistics becomes progressively poorer for long time-shifts (in particular, close to the glass-transition temperature $T_{\rm g}$), leading

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to larger error bars. [27,51] The method proposed in this paper is free of these difficulties and should allow for a rather facile calculation of the equilibrium moduli $L_{\mathrm{e}}(q)$ and $M_{\mathrm{e}}(q)$ (based on eqn (50) and (37)) using moderately long simulation runs like those required to obtain the standard structure factor $S(q)$ (*cf.* eqn (27)).

Furthermore, in the present section we generalized the classical equation for $L_{\mathrm{e}}(q)$ (*cf.* eqn (28)) to systems with mass polydispersity. The obtained results are valid for $q \neq 0$, including the regime $q \to 0$, where both the structure factors and the equilibrium moduli show well-defined limits, as argued in ref. 22. Noteworthily, eqn (50) derived above allows to calculate $M_{\mathrm{e}}(q)$ in the general case (including polydisperse systems with different types of particle dispersity).

4 General relation between the elasticity tensor and the stress correlation functions

As mentioned in the Introduction, we have recently derived a general relation between the stress correlation tensor, $C_{\alpha\beta\gamma\delta}(\underline{q},t)$, and the elasticity tensor, $E_{\alpha\beta\gamma\delta}\left(\underline{q},t\right)$ (see refs. 22,23). This relation reads

$$\breve{C}_{\alpha\beta\alpha'\beta'}(\underline{q},s) = \breve{E}_{\alpha\beta\alpha'\beta'}(\underline{q},s) - \frac{q_\delta q_\epsilon}{\rho_0 s^2}\breve{E}_{\alpha\beta\gamma\delta}(\underline{q},s)\breve{C}_{\gamma\epsilon\alpha'\beta'}(\underline{q},s), \qquad (51)$$

where the 'breve' sign indicates the Laplace–Carson transform [52] (known also as the 's-transform' [8,22,33]) of a time-dependent function $f(t)$,

$$\breve{f}\,(s) = s\int_0^\infty f\,(t)\,\mathrm{e}^{-\epsilon t}\mathrm{e}^{-st}\mathrm{d}t, \qquad (52)$$

and $\epsilon = 0^+$. In ref. 22, eqn (51) was obtained by considering a "no-flow constraint" imposing that $\vec{v}(\vec{q},t) = 0$ for all times $t < 0$, while for $t \geq 0$, the constraint is removed, allowing velocity fluctuations to occur again. Here we present a new derivation which does not involve any constraints. In particular, it is shown that eqn (51) follows from eqn (25) linking the generalized relaxation moduli with correlations of stress noise.

4.1 The relation for longitudinal components

Let us consider an amorphous system (*e.g.* a supercooled liquid) evolving in time with classical dynamics. The total stress field at wavevector $\underline{q}$, $\sigma_{\alpha\beta}(\underline{q},t)$, defined in eqn (13), is the sum of the time-dependent deterministic stress, $\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},t)$, and the stress noise, $\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},t)$, *cf.* eqn (22). Using the momentum equation (14) and eqn (18) and (23), we get the following relation between σ^{d} and σ in terms of their Fourier transforms (FTs) with respect to time, indicated solely by the argument, frequency ω, instead of t:

$$\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q},\omega) = \frac{\mathrm{i}}{\rho_0\omega}E_{\alpha\beta\gamma\delta}\left(\underline{q},\omega\right)\sigma_{\gamma\epsilon}(\underline{q},\omega)q_\epsilon q_\delta, \qquad (53)$$

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where $\alpha, \beta, \gamma, \ldots$ denote Cartesian components, $\underline{q}$ is the wavevector and $\rho_0 = \bar{m}c_0$ is the mean mass density. Here the FT of a t-dependent function $f(t)$ is defined as:

$$f(\omega) = \int_{-\infty}^{\infty} f(t) \exp(-\mathrm{i}\omega t) \mathrm{e}^{-\epsilon |t|} \mathrm{d}t, \tag{54}$$

where $\epsilon = 0^+$ is an infinitesimal positive number needed to impart convergence. [10]

Eqn (53) can be rewritten as [11]

$$\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q}, \omega) = \frac{1}{\rho_0 \omega^2} \breve{E}_{\alpha\beta\gamma\delta} \left(\underline{q}, s = \mathrm{i}\omega\right) \sigma_{\gamma\epsilon}(\underline{q}, \omega) q_\epsilon q_\delta, \tag{55}$$

where the 'breve' sign indicates the Laplace–Carson transform (52) of $E_{\alpha\beta\gamma\delta}\left(\underline{q}, t\right)$. In order to show that eqn (51) follows from eqn (25) it is instructive to start with a particular (simple but important) case when the wavevector $\underline{q}$ is oriented along axis 1, and we are interested only in longitudinal components of all tensors, like $L(q,t) \equiv E_{1111}(q,t)$ and $C_L(q,t) \equiv C_{1111}(q,t)$, *cf.* ref. 22 and 21. Using eqn (22) and (55) we get

$$\sigma^{\mathrm{n}}_{11}(\underline{q}, \omega) = \left[1 + \varkappa \breve{L}(q, s = \mathrm{i}\omega)\right] \sigma_{11}(\underline{q}, \omega), \text{ where } \varkappa \equiv q^2 / \left(\rho_0 s^2\right), \tag{56}$$

and the function $\breve{L}(q,s)$ is the Laplace–Carson transform (*cf.* eqn (52)) of the time-dependent longitudinal relaxation modulus $L(q,t)$.

In view of eqn (20) and (24), the Fourier transforms of C and C^{n} are (due to the Wiener–Khinchin theorem)

$$C_{\alpha\beta\alpha'\beta'}(\underline{q}, \omega) \simeq \frac{V}{T\Delta t} \left\langle \sigma_{\alpha\beta}(\underline{q}, \omega) \sigma_{\alpha'\beta'}(\underline{q}, \omega)^* \right\rangle, \tag{57}$$

$$C^{\mathrm{n}}_{\alpha\beta\alpha'\beta'}(\underline{q}, \omega) \simeq \frac{V}{T\Delta t} \left\langle \sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q}, \omega) \sigma^{n}_{\alpha'\beta'}(\underline{q}, \omega)^* \right\rangle, \tag{58}$$

where the star (*) means complex conjugate (note that $\sigma^*_{\alpha\beta}(\underline{q}, \omega) = \sigma_{\alpha\beta}(-\underline{q}, -\omega)$), $\Delta t = 1/\epsilon$ (*cf.* eqn (54)), and the above two equations become asymptotically exact for $\epsilon \to 0$, since both correlation functions, C and C^{n}, decay to 0 at $|t| \gg \tau_\alpha$, where τ_α is the terminal (α-relaxation) time.

On using the last 3 equations we obtain:

$$C^{\mathrm{n}}_L(q, \omega) \equiv C^{\mathrm{n}}_{1111}(q, \omega) = \left[1 + \varkappa \breve{L}(q, s)\right] \left[1 + \varkappa \breve{L}(q, -s)\right] C_L(q, \omega), \tag{59}$$

where $s = \mathrm{i}\omega$ (and $\omega \neq 0$ is real) here and below (until the end of section 4.2). Furthermore, on using also eqn (54) and (52) we find

$$\mathrm{i}\omega C_L(q, \omega) = \breve{C}_L(q, s) - \breve{C}_L(q, -s), \tag{60}$$

[10] More precisely, $\Delta t = 1/\epsilon$ can be treated as the sampling time that is assumed to be very long, much longer than the terminal relaxation time τ_α of the system, or formally $\Delta t \to \infty$ and $\epsilon \to 0$. More generally, the factor $\mathrm{e}^{-\epsilon|t|}$ in eqn (54) can be replaced by any real weight function $w_\epsilon(t)$ such that $w_\epsilon(t) \to 1$ at $\epsilon \to 0$ and $w_\epsilon(t) \to 0$ at $|t| \to \infty$; in this case $\Delta t = \int_{-\infty}^{\infty} w_\epsilon(t)^2 \mathrm{d}t$.

[11] Note that both $\sigma_{\gamma\epsilon}(\underline{q}, t)$ and $\sigma^{\mathrm{d}}_{\alpha\beta}(\underline{q}, t)$ can show high-frequency fluctuations.

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while, when additionally using eqn (25), we obtain

$$\mathrm{i}\omega C^{\mathrm{n}}_L(q,\omega) = \breve{L}(q,s) - \breve{L}(q,-s). \tag{61}$$

The above two relations allow to transform eqn (59) as

$$\breve{L}(q,s) - \breve{L}(q,-s) = \left[1+\varkappa\breve{L}(q,s)\right]\left[1+\varkappa\breve{L}(q,-s)\right]\left(\breve{C}_L(q,s) - \breve{C}_L(q,-s)\right). \tag{62}$$

The latter equation is always satisfied if

$$\breve{L}(q,s) = \left[1+\varkappa\breve{L}(q,s)\right]\breve{C}_L(q,s). \tag{63}$$

Note that the above equation, which is valid for $s = \mathrm{i}\omega$, defines C_L for a given $L(q,t)$. Importantly, there are no other solutions to eqn (62), since, in view of eqn (60) (and for a given L), it uniquely defines the Fourier transform $C_L(q,\omega)$ and therefore also both $C_L(q,t)$ and $\breve{C}_L(q,s)$. [12] Finally, note that eqn (63) is in harmony with eqn (51) for the longitudinal component of the stress autocorrelation function, $\breve{C}_{1111}(\underline{q},s) = \breve{C}_L(q,s)$. Therefore, we demonstrated that eqn (51) for the longitudinal components of $\breve{E}$ and $\breve{C}$ does follow from eqn (25). This result supports the general eqn (51).

4.2 The general case

Let us turn to the general case of the relation between the tensorial memory function $E_{\alpha\beta\alpha'\beta'}(\underline{q},t)$ and the tensor of stress correlation functions $C_{\alpha\beta\alpha'\beta'}(\underline{q},t)$. On using eqn (55) and (22) we get (for real $\omega \neq 0$ and $s = \mathrm{i}\omega$)

$$\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},\omega) = \mathcal{A}_{\alpha\beta\gamma\epsilon}(\underline{q},s)\sigma_{\gamma\epsilon}(\underline{q},\omega), \tag{64}$$

where

$$\mathcal{A}_{\alpha\beta\gamma\epsilon}(\underline{q},s) \equiv \delta_{\alpha\gamma}\delta_{\beta\epsilon} + \varkappa\breve{E}_{\alpha\beta\gamma\delta}\left(\underline{q},s\right)\hat{q}_\delta\hat{q}_\epsilon \tag{65}$$

and $\hat{\underline{q}} = \underline{q}/q$. Then, taking into account eqn (57) and (58), we obtain a relation between the correlation functions of the full stress and the stress noise:

$$C^{\mathrm{n}}_{\alpha\beta\alpha'\beta'}(\underline{q},\omega) = \mathcal{A}_{\alpha\beta\gamma\epsilon}(\underline{q},s)\mathcal{A}_{\alpha'\beta'\gamma'\epsilon'}(\underline{q},-s)C_{\gamma\epsilon\gamma'\epsilon'}(\underline{q},\omega), \tag{66}$$

Note that $\breve{E}_{\alpha\beta\gamma\delta}(\underline{q},-s) = \breve{E}^*_{\alpha\beta\gamma\delta}(\underline{q},s)$ for $s = \mathrm{i}\omega$ according to eqn (52), and hence $\mathcal{A}_{\alpha\beta\gamma\delta}(\underline{q},-s) = \mathcal{A}^*_{\alpha\beta\gamma\delta}(\underline{q},s)$. Furthermore, using eqn (25) and (18) we find (again for $s = \mathrm{i}\omega$)

$$sC^{\mathrm{n}}_{\alpha\beta\alpha'\beta'}(\underline{q},\omega) = \breve{E}_{\alpha\beta\alpha'\beta'}(\underline{q},s) - \breve{E}_{\alpha\beta\alpha'\beta'}(\underline{q},-s). \tag{67}$$

[12] This statement is rigorous if the factors in square brackets in eqn (62) are non-zero for any $s = \mathrm{i}\omega$ with real ω. The latter condition is indeed satisfied, since otherwise the lhs of eqn (62), which is proportional to the loss modulus $L''(q,\omega) \equiv \omega\int_0^\infty L(q,t)\cos(\omega t)\mathrm{d}t$, would vanish, which is impossible, since L'' must be positive. (This point is further discussed in section 4.2.) Therefore, $1+\varkappa\breve{L}(q,s) \neq 0$ which also means that eqn (63) defines a unique $\breve{C}_L(q,s)$ in terms of $\breve{L}(q,s)$.

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Eqn (66) can be considered as a linear matrix equation

$$C^{\mathrm{n}}_{\alpha\beta\alpha'\beta'}(\underline{q},\omega) = \mathcal{M}_{\alpha\beta\alpha'\beta'\gamma\epsilon\gamma'\epsilon'} C_{\gamma\epsilon\gamma'\epsilon'}(\underline{q},\omega), \tag{68}$$

where $\mathcal{M} = \mathcal{A}\mathcal{A}^*$ is given by the product of two $\mathcal{A}$-tensors in the rhs of eqn (66) defining C^{n} in terms of C. For a given C^{n} eqn (68) can be solved for C using the standard linear algebra, so that eventually (also taking into account eqn (67)) the stress correlation tensor C can be expressed in terms of the generalized relaxation moduli, E. More precisely, this is true if the solution of eqn (68) for C is unique which means that the matrix $\mathcal{M}$ is not degenerate. In other words, for any nonzero 4th-rank tensor C, $\mathcal{M} \cdot C$ is also nonzero. To prove this statement let us assume the opposite: There exists a $C \neq 0$ such that $\mathcal{M} \cdot C = 0$. The latter assumption implies that either $X \equiv \mathcal{A}^* \cdot C = 0$ or, else, $X \neq 0$ but $\mathcal{A} \cdot X = 0$. Let us consider the second option, $\mathcal{A} \cdot X = 0$ (the reasoning for $\mathcal{A}^* \cdot C = 0$ is analogous):

$$\mathcal{A}_{\alpha\beta\gamma\epsilon}(\underline{q},s) X_{\alpha'\beta'\gamma\epsilon} = 0. \tag{69}$$

As $X \neq 0$, there exist two indices α', β' such that $Y_{\gamma\epsilon} \equiv X_{\alpha'\beta'\gamma\epsilon}$ is non-zero, while $\mathcal{A} \cdot Y = 0$. Then, imposing that $\sigma_{\gamma\epsilon}(\underline{q},\omega) = \mathrm{const}\, Y_{\gamma\epsilon}$ in eqn (64) we find that $\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},\omega) = 0$. Therefore, we arrive at the dynamical state with a stress fluctuation wave (with frequency ω and wavevector $\underline{q}$) which stays forever without decay, since eqn (64) in this case says that the mechanical balance is maintained by the deterministic stress only. It means that there is no dissipation in this dynamical state, which is impossible according to the basic principle of thermodynamics, stating that the dissipation rate $\mathcal{D}$ must be positive in a non-equilibrium system (like the system we consider which shows permanent oscillations), hence the entropy of any such thermally isolated system must increase in time (according to the second law of thermodynamics). Therefore, $\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},\omega) = 0$ is not allowed (for any $q \neq 0$, $\omega \neq 0$).

This conclusion is also in line with the fact that a noise, the stress noise in the present case, is intimately related to the dissipation and friction (*cf.* Appendix A). Noteworthily, eqn (87) in Appendix A proves that the energy dissipation rate $\mathcal{D}$ cannot be negative (in a system perturbed by an external force). To sum up, the above physical argument ensures that the matrix $\mathcal{M}$ is not degenerate and so eqn (68) defines a unique C in terms of C^{n} and E.

Let us now proceed with the derivation of eqn (51). Taking into account that the Fourier transform of the full stress correlation function is (*cf.* eqn (60)),

$$C_{\alpha\beta\gamma\delta}(\underline{q},\omega) = \frac{1}{s}\left[\breve{C}_{\alpha\beta\gamma\delta}(\underline{q},s) - \breve{C}_{\alpha\beta\gamma\delta}(\underline{q},-s),\right] \tag{70}$$

with $s = \mathrm{i}\omega$ and real $\omega \neq 0$ as before, and using eqn (67) we rewrite eqn (66) as

$$\breve{E}_{\alpha\beta\alpha'\beta'}(\underline{q},s) - \breve{E}_{\alpha\beta\alpha'\beta'}(\underline{q},-s) = \mathcal{A}_{\alpha\beta\gamma\epsilon}(\underline{q},s)\mathcal{A}_{\alpha'\beta'\gamma'\epsilon'}(\underline{q},-s)\left[\breve{C}_{\gamma\epsilon\gamma'\epsilon'}(\underline{q},s) - \breve{C}_{\gamma\epsilon\gamma'\epsilon'}(\underline{q},-s)\right]. \tag{71}$$

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Replacing the $\mathcal{A}$-factors in the above equation with expressions in the rhs of eqn (65) and omitting (as a trial) in the resultant equation all terms with the second argument '$-s$' we get:

$$\breve{E}_{\alpha\beta\alpha'\beta'}(\underline{q}, s) = \mathcal{A}_{\alpha\beta\gamma\epsilon}(\underline{q}, s)\breve{C}_{\gamma\epsilon\alpha'\beta'}(\underline{q}, s), \tag{72}$$

and an equivalent equation can be obtained by omitting all terms with argument s in eqn (71). [13] Furthermore, one can easily show (using the major symmetries of C and E tensors) that, if eqn (72) is valid, the basic eqn (71) is satisfied. Taking also into account that for the reasons as presented below eqn (68), eqn (71) has a unique solution (defining the C-tensor once the elasticity tensor E is given). Since for similar reasons the same is true for eqn (72), we deduce that the unique solution of the basic eqn (71) must also satisfy eqn (72) which can be written in a more explicit form as:

$$\breve{C}_{\alpha\beta\alpha'\beta'}(\underline{q}, s) = \breve{E}_{\alpha\beta\alpha'\beta'}(\underline{q}, s) - \frac{q_\delta q_\epsilon}{\rho_0 s^2}\breve{E}_{\alpha\beta\gamma\delta}(\underline{q}, s)\breve{C}_{\gamma\epsilon\alpha'\beta'}(\underline{q}, s),$$

where the 'breve' sign indicates the Laplace–Carson transform.

To conclude, we thus proved, without invoking any constraints on the flow field (which were employed in ref. 22 and 23), that eqn (51) indeed follows from eqn (25) which was discussed in section 2.2. Eqn (51) and (25) are therefore generally valid for all equilibrated amorphous systems with time-translational invariant Newtonian dynamics, as anticipated in ref. 21, 22 and 23.

It is worth noting that the above derivation is applicable also to polydisperse systems—in particular those with mass or size polydispersity of particles—and to systems with arbitrary thermal conductivity, including isothermic and adiabatic systems as the limiting cases.

5 Discussion and Summary

1. Why the velocity field should be defined with mass factors.

In the present paper we used the mass factors to define the velocity, strain rate and concentration fields, *cf.* eqn (6), (16) and (5). These definitions differ from the so-to-say 'conventional' (or 'standard') definitions of these fields, not involving the mass factors. [25,28] We mentioned this issue at the end of section 3.5. Its more detailed discussion is presented below.

(i) According to eqn (17), the tensor of elastic moduli $E_{\alpha\beta\gamma\delta}(\underline{q}, t)$ depends on how the velocity field, $v_\alpha(\underline{r}, t)$, and the related strain rate, $\dot{\gamma}_{\alpha\beta}(\underline{r}, t) = \partial v_\alpha(\underline{r}, t)/\partial r_\beta$, are defined. Our point is that in the general case the velocity field and concentration field must be defined respectively as in eqn (6) and (5) with the mass factors, $m_i/\bar{m}$, instead of the 'standard' definition of the velocity field,

$$\underline{v}^{\rm st}(\underline{r}, t) = \frac{1}{c_0}\sum_i \underline{v}_i(t)\delta(\underline{r} - \underline{r}_i(t)), \tag{73}$$

[13] Note that eqn (72) is a conjecture. It can be justified in the following way: As explained below, eqn (71) does follow from eqn (72). Therefore, given that both eqn (71) and (72) have a unique solution, they must be equivalent.

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and the microscopic concentration,

$$c^{\mathrm{st}}(\underline{r},t) = \sum_i \delta(\underline{r} - \underline{r}_i(t)). \tag{74}$$

The above equations obviously become equivalent to eqn (6) and (5) in the case of equal mass of all particles. The most important arguments in favor of eqn (5) and (6) are presented below:

• For systems composed of particles with different masses (m_i) the definition of the velocity field as in eqn (6) is widely accepted. [29,31,53] Consistency with the mass balance equation (4) then requires the concentration field to be defined as in eqn (5).

• Let us consider as an example a polydisperse oligomer melt [1] treating each chain as a 'particle'. In this case, eqn (74) would provide the chain-number concentration field. Is it appropriate to define a generalized q-dependent longitudinal modulus $L(q,t)$ in terms of such a concentration field? The answer is probably 'no', given that $c^{\mathrm{st}}(\underline{r},t)$ is expected to strongly fluctuate, as one chain of, say, 10 units may be replaced by 2 chains of 5 units, thus increasing the local chain number concentration c^{st} by a factor of ~ 2. It is clear that such a strong fluctuation should not be related to the compressibility of the system. Such a problem is avoided if the contribution of each chain is scaled with its molecular mass, thus leading to the definitions of $c(\underline{r},t)$ and $\underline{v}(\underline{r},t)$ as given by eqn (5) and (6).

• Another way to come to the same conclusion is as follows: Consider a mixture of small spherical beads (unimers of mass m) and dimers (two beads of total mass $2m$ connected by an ideal spring with elastic constant k). At low k, the beads in a dimer are far apart so that it is natural to postulate that the velocities of both beads of a dimer must contribute on the equal basis with a unimer bead velocity in the collective velocity field $\underline{v}(\underline{r},t)$, which is in accordance with eqn (6) we adopted. As k increases, the beads of a dimer stay closer to each other, but there is no reason for the dimer velocities to suddenly get weighted twice lighter for high dimer rigidities. Hence our definition, eqn (6), must be appropriate in this case as well.

(ii) The dynamics of supercooled glass-forming liquids and other complex fluids (including flow, deformation and sound waves) are largely defined by the microscopic internal stress field, $\sigma_{\alpha\beta}$, as well as the mass density, ρ, and mass current density, $\underline{J} = \rho_0 \underline{v}$. Importantly, all these fields are related by the general conservation laws, *cf.* eqn (4) and (11). It is therefore natural to define the elastic moduli in terms of these fields: In this case, the important relations between the moduli and correlation functions of microscopic fields (like eqn (63) known from the classical theory developed for monodisperse systems [28]) stay valid also in the more general case of mass polydispersity. Hence, for example, the strain rate field must be defined in terms of the generalized collective velocity proportional to the momentum density (*cf.* eqn (16) and (6), and ref 8, 22 and 23). If the strain field is defined from this velocity field, it naturally involves the mass factors, too. [31]

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To reiterate this point, the classical theories of fluid dynamics actually follow the ideas mentioned above, [25,26,28,54] however then they mostly focus on the case of particles with equal mass, implying that eqn (73) and (74) appear naturally.

(iii) To impose a generalized (non-uniform) deformation on an amorphous system it is necessary to apply an appropriate external force field acting on all particles. [8,22] In the case of a deformation wave with wavevector $\underline{q}$ the force on a particle 'i' is:

$$\underline{F}_i(t) = m_i \underline{A}(t) \mathrm{e}^{\mathrm{i}\underline{q}\cdot\underline{r}_i(t)} + \mathrm{c.c.}, \tag{75}$$

where $\underline{A}(t)$ is an acceleration and c.c. means complex conjugate. It is due to the mass factors m_i that a coherent acceleration of all particles is provided by the external forces. It is also noteworthy that the standard definitions of the relaxation moduli, $E_{\alpha\beta\gamma\delta}(\underline{q}, t)$, are hinged on the instantaneous canonical transformations in the Hamiltonian phase space [21,51,55] whose effect can be exactly reproduced by application of appropriate perturbative external forces involving the very mass factors that are present in eqn (75). [21,22]

Importantly, application of $\underline{F}_i(t)$ to each particle defined in eqn (75) leads to the following rate-of-change of the total energy H of the system:

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \sum_i \underline{F}_i(t) \cdot \underline{v}_i(t) = V \underline{A}(t) \cdot \underline{J}(-\underline{q}, t) + \mathrm{c.c.}, \tag{76}$$

where eqn (9) was used to obtain the last equality. Eqn (76) shows that, if the strain rate $\dot{\gamma}_{\alpha\beta}(\underline{q}, t)$ is defined via eqn (16) with the microscopic velocity field of eqn (6) and (8), the no-strain condition, $\dot{\gamma}_{\alpha\beta}(\underline{q}, t) = 0$, automatically implies that $H = \mathrm{const}$, as it should be in the case of zero strain.

2. Why mass polydispersity is important for static elasticity at $q \neq 0$.

As shown in section 3, both equilibrium moduli, $L_\mathrm{e}(q)$ and $M_\mathrm{e}(q)$, depend not only on the interaction potentials between the particles but also on their masses. One may ask why the particle masses have anything to do with the static properties of a liquid. Indeed, the particle masses are not relevant, for example, for the bulk isothermal compressibility associated with the pressure response to a uniform affine compression of the system, *cf.* eqn (30) (see also refs. [56,57]). However, the situation is different in the case of q-dependent properties of *polydisperse* systems: a particle size dispersity can lead to a strong impact also on the static q-dependent moduli, even if the polydispersity index (PDI) is low (like PDI $\sim 1\%$) [8,43], in contrast to the bulk static moduli. A similar effect is expected for systems with mass polydispersity which is normally associated with dispersities of both particle size and interaction potential.

The important point here is that in order to obtain a generalized q-dependent modulus (*e.g.* $L(q, t)$ or $M(q, t)$) it is necessary to create a deformation *wave*, and this cannot be done by applying pressure only at the surface of the system (like in the case of a uniform compression). Instead, it is necessary to apply an appropriate external force field, so that a force on each particle is proportional

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to its mass (see eqn (75) and point 1(ii) above), and hence the external potential energy of a particle depends not only on its coordinates, but also on its mass (not to mention that in the case of, say, transverse deformation the external force cannot be generated by a potential energy field). That is why the fact that without external forces particle momenta can be integrated out of the partition function (leading to a thermodynamic potential depending only on particle configurations) is irrelevant for q-dependent elastic moduli even in the static case: the static moduli do depend on particle masses.

It is also important that in the general case of the particle mass and size polydispersity, the multi-component nature of the system leads to a slow inter-diffusion of particles according to their mass/size: In spite of the strain wave being kept constant, small and large (light and heavy) particles tend to partially separate and redistribute. [43,58] For a size-polydisperse two-dimensional Lennard–Jones system this process was elucidated in detail in ref. 8 (see section II.F there). In this case, the initially homogeneous local *composition* of the system slowly becomes modulated, since large particles tend to escape from denser regions, being replaced there by smaller particles which penetrate more easily into regions of higher pressure. [8] As a result, the *equilibrium* (*i.e.* genuinely static) elastic moduli, $L_\mathrm{e}(q)$ and $M_\mathrm{e}(q)$—which are the long-time limit of $L(q,t)$ and $M(q,t)$, *cf.* eqn (26)—become dependent on the particle mass/size distribution and significantly different from the bulk moduli even for very low q.

To reiterate the point on the *bulk* moduli which correspond to essentially *affine* deformations: In this case, no external force $\underline{F}_i(t)$ [*cf.* eqn (75)] is needed to maintain a constant affine strain, and that is why, say, the modulus $L_\mathrm{e}^\mathrm{bulk}$ [see eqn (30)] does not depend on particle masses (m_i) in contrast to $L_\mathrm{e}(q)$ which is generally different from $L_\mathrm{e}^\mathrm{bulk}$ in polydisperse systems, as explained above and in ref. 8 (and also mentioned below eqn (30)).

3. As established in ref. 22, the equilibrium elasticity tensor $E^\mathrm{e}_{\alpha\beta\gamma\delta}(\underline{q})$, which represents the genuinely static limit of the tensor $E_{\alpha\beta\gamma\delta}(\underline{q},t)$ of generalized relaxation moduli, can be expressed in terms of two elastic moduli, longitudinal $L_\mathrm{e}(q)$ and transverse $M_\mathrm{e}(q)$. In section 3 we formulated a new approach allowing to obtain these equilibrium moduli based on structural correlation properties of the system (*i.e.* on correlations taken at the same time). The main results are eqn (37) and (50) defining the moduli in terms of several structure factors. This approach opens up a way for a faster and more precise calculation of the equilibrium moduli using MD simulations (*cf.* section 3.5). It is worth emphasizing that eqn (37) and (50) are generally valid, also for polydisperse systems, as discussed in section 3.5.

4. We derived and discussed the basic general relations between the elasticity tensor $E_{\alpha\beta\gamma\delta}(\underline{q},t)$ and the stress correlation function $C_{\alpha\beta\gamma\delta}(\underline{q},t)$ for equilibrium amorphous systems. We employed eqn (25) in order to elaborate a conceptually new derivation of the basic relation, eqn (51), which does not involve consideration of either the constrained dynamics (implying application of external forces) or non-steady flow conditions, as originally employed in ref. 22 to obtain eqn (51).

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The general derivation presented in section 4 implies that the resultant eqn (51) is applicable also to polydisperse systems with any kind of polydispersity and with a finite thermal conductivity, including extreme cases of isothermic and adiabatic conditions.

5. Note that application of eqn (25) generally requires isolation of the stress noise from the total stress by eliminating the deterministic stress part at all times, *e.g.* via an appropriate force field imposing the no-flow constraint, $\underline{v}(\underline{q},t)=0$, for all t. We plan to return to this problem in near future.

The final remarks concerning the stress noise, $\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},t)$: Importantly, this noise is coming from structural, compositional and enthalpic thermal fluctuations which are omnipresent. Hence, the stress noise must also exist in a system where the flow is suppressed, $\underline{v}(\underline{q},t)=0$, by a suitably chosen external constraint. Perhaps an analogy with thermodynamics would be helpful to better understand the physical meaning of $\sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},t)$. The pressure of a one-component, single-phase system is a function of concentration $c=N/V$ and temperature T. Even if the volume is fixed, corresponding to no deformation or in our case $\underline{v}(\underline{q},t)=0$, the pressure can still change due to variations of T. A similar mechanism should also exist for the tensorial stress fluctuations giving rise to the concept of stress noise.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. All the relevant data generated during this study have been included in this published article.

Conflicts of interest

There are no conflicts to declare.

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A On the dissipation rate and its relation to the stress noise

Let us consider a liquid near the equilibrium state which is perturbed by a weak external force per volume, $\underline{f}_{\mathrm{ext}}=\rho_0\underline{A}(\underline{r},t)+\mathrm{c.c.}$, where the acceleration $\underline{A}(\underline{r},t)$ is defined as [*cf.* eqn (75)]

$$\underline{A}(\underline{r},t)=\tilde{\underline{A}}\exp(\mathrm{i}\underline{q}\cdot\underline{r}+\mathrm{i}\omega t). \tag{77}$$

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Such an external force generates a weak flow with velocity

$$\underline{v}(\underline{r},t) = \underline{\tilde{v}}\exp(\mathrm{i}\underline{q}\cdot\underline{r} + \mathrm{i}\omega t) + \text{c.c.}, \tag{78}$$

where $\underline{\tilde{A}}$ and $\underline{\tilde{v}}$ are complex vectors. The external force and flow velocity are related due to the momentum equation [*cf.* eqn (14)]

$$\mathrm{i}\omega\tilde{v}_\alpha = \tilde{A}_\alpha + \tilde{\sigma}_{\alpha\beta}\mathrm{i}q_\beta/\rho_0 \tag{79}$$

where $\sigma_{\alpha\beta}(\underline{r},t) = \tilde{\sigma}_{\alpha\beta}\exp(\mathrm{i}\underline{q}\cdot\underline{r} + \mathrm{i}\omega t) + \text{c.c.}$ is the mean (ensemble averaged) stress field, which is therefore deterministic, $\sigma_{\alpha\beta}(\underline{r},t) = \sigma^{\mathrm{d}}_{\alpha\beta}(\underline{r},t)$. Note that 'tilde' in the above equations indicates complex amplitudes (corresponding to the selected $\underline{q}$ and ω), and that 'tilde' is omitted in what follows.

The dissipation rate $\mathcal{D}$ is equal to the work per time (and per volume) performed by the external force:

$$\mathcal{D} = \rho_0\underline{A}\cdot\underline{v}^* + \text{c.c.} \tag{80}$$

Using eqn (79) the acceleration $\underline{A}$ can be expressed in terms of $\underline{v}$ and $\sigma_{\alpha\beta} = \sigma^{\mathrm{d}}_{\alpha\beta}$:

$$A_\alpha = \mathrm{i}\omega v_\alpha - \sigma_{\alpha\beta}\mathrm{i}q_\beta/\rho_0. \tag{81}$$

The $\underline{v}$ contribution to $\underline{A}$ in the above equation does not give rise to any dissipation (by virtue of eqn (80)), while the second term in the rhs of eqn (81), involving $\sigma_{\alpha\beta}$, can again be expressed in terms of the flow velocity field [*cf.* eqn (23)]:

$$\sigma_{\alpha\beta} = E_{\alpha\beta\gamma\delta}(\underline{q},\omega)\mathrm{i}v_\gamma q_\delta, \tag{82}$$

where $E_{\alpha\beta\gamma\delta}(\underline{q},\omega)$ is the Fourier transform [*cf.* eqn (54)] of the tensor function $E_{\alpha\beta\gamma\delta}(\underline{q},t)$ of the generalized relaxation moduli. Thus, we get

$$\mathcal{D} = E_{\alpha\beta\gamma\delta}(\underline{q},\omega)q_\beta q_\delta v^*_\alpha v_\gamma + \text{c.c.} \tag{83}$$

According to eqn (25) the Fourier transform [eqn (54)] of the E-tensor can be represented as (for $\epsilon \to 0$):

$$E_{\alpha\beta\gamma\delta}(\underline{q},\omega) = \frac{1}{\mathrm{i}\omega}E^{\mathrm{e}}_{\alpha\beta\gamma\delta}(\underline{q}) + \int_0^\infty C^{\mathrm{n}}_{\alpha\beta\gamma\delta}(\underline{q},t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t. \tag{84}$$

It is straightforward to show that only the real part of E does contribute to $\mathcal{D}$ in eqn (83). Therefore, by taking into account that C^{n} is even in time we get:

$$\mathcal{D} = C^{\mathrm{n}}_{\alpha\beta\gamma\delta}(\underline{q},\omega)q_\beta q_\delta v^*_\alpha v_\gamma. \tag{85}$$

Finally, on using eqn (58) and defining

$$X(\underline{q},\omega) \equiv \sigma^{\mathrm{n}}_{\alpha\beta}(\underline{q},\omega)v^*_\alpha q_\beta, \tag{86}$$

we obtain the dissipation rate

$$\mathcal{D} = \frac{V\epsilon}{T}\left\langle X(\underline{q},\omega)X^*(\underline{q},\omega)\right\rangle, \tag{87}$$

which is obviously necessarily non-negative. Note that $\mathcal{D}$ stays finite in the limit $\epsilon \to 0$ where $\epsilon = 1/\Delta t$ (*cf.* eqn (58) and the sentence below it).

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B Derivation of the generalized compressibility equation based on cross-correlations of stress and concentration

The longitudinal modulus $L_{\mathrm{e}}(q)$ defines the static response of the longitudinal stress $\delta\sigma_{11}(\underline{q})$ to a weak permanent (time independent) strain, $\delta\gamma(\underline{q})$, [22,23] applied to each microstate of a canonical equilibrium ensemble at $t=-\infty$, [14]

$$\delta\gamma(\underline{q}) \equiv \delta\gamma_{11}(\underline{q}) = \mathrm{i}q\delta u_1(\underline{q}), \tag{88}$$

where $\delta u_1(\underline{q})$ defines the field of particle displacements parallel to $\underline{q}$, $\delta u_1(\underline{r}) = \delta u_1(\underline{q})\mathrm{e}^{\mathrm{i}\underline{q}\cdot\underline{r}} + \text{c.c.}$, applied to all microstates. [22] [15] Thus, the ensemble-averaged stress response is (see section 6.2 in ref. 22 and eqn (31) and (32) in ref. 23)

$$\delta\sigma_{11}(\underline{q}) = L_{\mathrm{e}}(q)\delta\gamma(\underline{q}). \tag{89}$$

Recalling that for weak deformations the rate-of-change of the collective displacement is equal to the collective velocity $\underline{v}(\underline{q},t)$, [31]

$$\frac{\partial\underline{u}(\underline{q},t)}{\partial t} = \underline{v}(\underline{q},t), \tag{90}$$

and using eqn (10) we get

$$\delta c(\underline{q})/c_0 = -\mathrm{i}q\delta u_1(\underline{q}) = -\delta\gamma(\underline{q}), \tag{91}$$

where $\delta c(\underline{q})$ is the concentration change generated by a weak longitudinal collective displacement $u_1(\underline{q})$. Using eqn (91) we can rewrite eqn (89) as

$$\delta\sigma_{11}(\underline{q}) = -L_{\mathrm{e}}(q)\delta c(\underline{q})/c_0, \tag{92}$$

which means that $L_{\mathrm{e}}(q)$ also defines the static longitudinal stress response to a concentration perturbation (see also eqn (34) and (32) of ref. 23).

Noteworthily, a permanent concentration perturbation can be created by a weak static external field (*i.e.* with U_0 being infinitesimal),

$$U^{(i)}_{\mathrm{ext}}(\underline{r}) = -\frac{m_i}{\bar{m}V}U_0\mathrm{e}^{\mathrm{i}\underline{q}\cdot\underline{r}}, \tag{93}$$

which is applied to each particle i. This gives rise to a perturbative term in the total Hamiltonian ($\mathcal{H} = \mathcal{H}_0 + \Delta\mathcal{H}$ where $\mathcal{H}_0$ is the unperturbed Hamiltonian) of the system:

$$\Delta\mathcal{H} = \sum_i U^{(i)}_{\mathrm{ext}}(\underline{r}_i) = -U_0 c^*(\underline{q}), \tag{94}$$

[14]Note that $q \neq 0$ here and below, and we use the naturally rotated coordinates (NRC) with axis 1 parallel to the wavevector $\underline{q}$. [21,22,33]

[15]Note that the strain tensor in the real space is defined as $\gamma_{\alpha\beta} = \frac{\partial u_\alpha}{\partial r_\beta}$.

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where we used eqn (7) and the fact that the mean $c(\underline{q})$ vanishes for the unperturbed equilibrium system. The perturbation $\Delta\mathcal{H}$ changes the distribution of microstates $\mathit{\Gamma}$ as

$$\mathcal{P}(\mathit{\Gamma}) = \mathcal{P}_0(\mathit{\Gamma})\left(1 - \frac{\Delta\mathcal{H}}{T}\right), \qquad \mathcal{P}_0(\mathit{\Gamma}) = \text{const}\,\mathrm{e}^{-\mathcal{H}_0/T}, \tag{95}$$

which implies that the emsemble-averaged longitudinal stress response generated by the external field is given by (note that the mean $\sigma_{11}(\underline{q})$ is zero in the unperturbed reference state)

$$\delta\sigma_{11}(\underline{q}) = \int \sigma_{11}(\underline{q}|\mathit{\Gamma})\mathcal{P}(\mathit{\Gamma})\mathrm{d}\mathit{\Gamma} = -\frac{1}{T}\left\langle \sigma_{11}(\underline{q})\Delta\mathcal{H}\right\rangle = \frac{U_0}{T}\left\langle \sigma_{11}(\underline{q})c^*(\underline{q})\right\rangle, \tag{96}$$

where $\sigma_{11}(\underline{q}|\mathit{\Gamma})$ means the longitudinal stress fluctuations at $\underline{q}$ under the condition that the system is in the microstate $\mathit{\Gamma}$, $\langle\ldots\rangle$ denotes the equilibrium ensemble average calculated with $\mathcal{P}_0$, and eqn (94) was inserted to obtain the last equality in eqn (96).

There is an alternative way to determine $\delta\sigma_{11}(\underline{q})$ in terms of U_0. As we consider the static case, the mean, time-averaged, force on each volume element must be zero. By virtue of the momentum balance equation [*cf.* eqn (11)] this implies

$$\frac{\partial\sigma_{\alpha\beta}}{\partial r_\beta} + f_\alpha^{\text{ext}} = 0, \tag{97}$$

where

$$f_\alpha^{\text{ext}}(\underline{r}) = -\frac{1}{V}\frac{\partial}{\partial r_\alpha}\sum_i U_{\text{ext}}^{(i)}(\underline{r}) = \frac{1}{V}c_0 U_0 \mathrm{i} q_\alpha \mathrm{e}^{\mathrm{i}\underline{q}\cdot\underline{r}} \tag{98}$$

is the average external force per volume at position $\underline{r}$ of volume element considered (note that the prefactor $1/V$ in eqn (98) is the probability density that a particle i is present near the position $\underline{r}$). Specifying eqn (97) and (98) for the longitudinal component ($\alpha = 1$) we get the time-averaged perturbation of the stress σ_{11}:

$$\delta\sigma_{11}(\underline{r}) = -c_0\frac{U_0}{V}\mathrm{e}^{\mathrm{i}\underline{q}\cdot\underline{r}},\ \delta\sigma_{11}(\underline{q}) = -c_0\frac{U_0}{V}. \tag{99}$$

On comparing eqn (99) with eqn (96) we finally obtain

$$\left\langle \sigma_{11}(\underline{q})c^*(\underline{q})\right\rangle = -\frac{c_0 T}{V}. \tag{100}$$

This equation agrees with the result obtained in ref. 23 (*cf.* eqn (39), (38), (32) and (33) in this reference). It is worth noting that eqn (100) is generally valid, also for polydisperse systems including those with mass polydispersity, provided that the local concentration is defined in eqn (5) involving mass-dependent weight factors.

Eqn (100) is a specific example of an equilibrium correlation function for two $\underline{q}$-dependent variables. Let us consider the case where A and B denote any two $\underline{q}$-dependent variables. We can always write

$$A = \lambda B + X, \tag{101}$$

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where λ is an unknown number and X is independent of B, implying that $\langle XB^* \rangle = 0$ and $\langle XB \rangle = 0$ (note that $\langle XB \rangle = 0$, $\langle BB \rangle = 0$ are valid since both X and B correspond to a non-zero $\underline{q}$ and the equilibrium system we consider is macroscopically uniform). Taking into account that for a large system the variables A and B are small fluctuations which are jointly Gaussian (and therefore the same is true for X) we conclude (based on the above equations) that the conditional average of X for any prescribed value of B, $\langle X \rangle_B$, always vanishes. Hence λ is the ratio of two correlators,

$$\lambda = \frac{\langle AB^* \rangle}{\langle BB^* \rangle} \tag{102}$$

For $A = \sigma_{11}(\underline{q})$ and $B = c(\underline{q})$, and with the help of eqn (92) and eqn (101) we therefore identify λ as

$$\lambda = -L_{\mathrm{e}}(q)/c_0. \tag{103}$$

Furthermore, in this case we have

$$\langle BB^* \rangle = \left\langle c(\underline{q})c^*(\underline{q}) \right\rangle = \frac{N}{V^2} S_2(q), \tag{104}$$

where $S_2(q)$ is the structure factor defined in eqn (32) for the general case of particle mass polydispersity, which is different from the standard structure factor $S(q)$ [*cf.* eqn (27)].

Using eqn (100), (102),(103), and (104) we finally get the generalized compressibility equation [*cf.* eqn (37)]:

$$L_{\mathrm{e}}(q) = c_0 T / S_2(q). \tag{105}$$

This result agrees with the theory presented in ref. 22.

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Data availability

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The data that support the findings of this study are available from the corresponding author upon reasonable request. All the relevant data generated during this study have been included in this published article.