Hydrodynamics of isotropic ferrogels

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We derive the complete set of macroscopic dynamic equations for ferrogels under an external magnetic field, including the magnetization as an independent dynamic degree of freedom. The magnetoelasticity comes in the form of magnetostriction and through the magnetic part of the Maxwell stress. Various dynamic couplings of the elastic degree of freedom with the magnetization and the magnetic field are found. We discuss static elongation, shear deformations, and the modified sound spectrum in the presence of an external magnetic field.

I. INTRODUCTION

Ferrogels belong to a new class of magnetocontrolled elastic materials, which are chemically cross-linked polymer networks swollen with a ferrofluid. Coupling the elastic medium with the magnetic properties of the particles allows us to manipulate the elastic behavior of ferrogels by external magnetic fields and/or field gradients. This feature offers opportunities for various applications as, e.g., soft actuators, micromanipulators, and artificial muscles [1]. Heating of these materials in alternating magnetic fields is a promising approach in cancer therapy [2]. Since the magnetic rubber is soft, inexpensive, and controlled in its properties by the magnetic field, it can also be used in an apparatus for immunoblotting [3].

The properties of ferrogels depend on the preparation conditions (solvent, concentration of cross linking, concentration of magnetic particles). Preparing ferrogels in an external magnetic field one can obtain large columns of magnetic particles, the length of which is much larger than the mesh size of the network. In this case the clusters are fixed in the network [4]. As a result the ferrogel is strongly anisotropic [5].

Here we consider isotropic ferrogels. The typical size of the magnetic particles is ∼ 10 nm. The bare particles tend to coagulate. To prevent this, magnetic grains are charged [6] or coated by polymers [7]. The magnetic gels are usually only weakly cross linked, so that the size of the magnetic particles is much smaller than the mesh size of the network. However, still some coagulation takes place resulting in magnetic clusters comparable in size to that of the mesh [8]. Without external field no remnant magnetization is found. An external field easily magnetizes the sample (superparamagnetism). Outside equilibrium the magnetization relaxes to its equilibrium value and orientation set by the external field. This relaxation is rather slow compared to the (many) microscopic relaxation processes and it is therefore reasonable to keep the magnetizations as a macroscopic, slowly relaxing variable.

In inhomogeneous magnetic fields an abrupt shape transition of isotropic ferrogels was observed [8]. The force generated by such a magnetic gradient field drives the magnetic grains in the direction of the gradient, thus deforming the network, if there is a coupling between the magnetic particles and the network. In these experiments this seems to be the case. Therefore, we assume in our model that the magnetic particles are "attached" to the network, although the precise meaning of this statement is unclear on the molecular level. On the macroscopic level this leads to a coupling of rotations of the magnetization as well as changes of its absolute value with the elastic strains or stresses. In particular, we will discuss static elongation, shear deformations, and the modified sound spectrum in a homogeneous magnetic field by solving the appropriate generalized hydrodynamic equations.

To derive the macroscopic dynamic equations we use the hydrodynamic method. Hydrodynamics describes a system in the long wavelength limit and for long time scales. The hydrodynamic equations are derived by means of symmetry and thermodynamic arguments. The main advantage of the hydrodynamic method lies in its generality, which allows its application to very different systems. However, the occurrence of phenomenological parameters in the static and dynamic expansions are the price one has to pay for this generality. Therefore coefficients turning up in the equations below have to be determined by microscopic models or by experiments.

There are cases, where nonhydrodynamic, relaxing processes become so slow that their dynamics takes place on a macroscopic time scale as well. Then it is appropriate to also include nonhydrodynamic, but slowly relaxing variables in the dynamic description of such a system. In ferrofluids the magnetization (its orientation as well as its absolute value) relaxes to the equilibrium value set by the external field. The appropriate relaxation time is much larger than all microscopic time scales and can be relevant for the macroscopic dynamics [9,16]. In this case one should treat the magnetization as an additional dynamic variable with its own dynamical (relaxation) equation.

Here we generalize the set of hydrodynamic equations for ordinary gels to those for ferrogels by including the magnetization as an additional, slowly relaxing variable. Special emphasis is laid on the magnetomechanical cross couplings between elasticity and the magnetic degree of freedom. As an application for these equations we discuss the spectrum of

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longitudinal and transverse sound in the presence of an external magnetic field. In the low frequency limit a comparison with static elastic measurements is made. A possible way of exciting shear waves by oscillating temperature gradients in the presence of a gradient field is outlined.

II. STATICS AND THERMODYNAMICS

The macroscopic description of a system starts with the identification of the relevant variables. Apart from the quantities that are related to local conservation laws, such as mass density ρ, momentum density g, energy density ε, and concentration c of the swelling fluid (and/or that of the magnetic particles), we consider the elastic strain u_{ij} and the magnetization M as additional variables. In a crystal the former is related to the broken translational symmetry due the long range positional order, which gives rise to the displacement vector $\vec{u}$ as a hydrodynamic symmetry variable. Since neither solid body translations nor rigid rotations give rise to elastic deformations, the strain tensor is used as a variable, which reads in linearized version $u_{ij} = \frac{1}{2}(\nabla_i u_j + \nabla_j u_i)$. In amorphous solids, such as rubbers, gels, etc., linear elasticity is still described by a second-rank, symmetric strain tensor. For a proper description of nonlinear elasticity cf. [10]. For the purpose of this work, however, linear elasticity is sufficient. As discussed in the Introduction, the magnetization M is a slowly relaxing variable in the superparamagnetic case.

Assuming local thermodynamic equilibrium, i.e., all microscopic, fast relaxing quantities are already in equilibrium, we have the Gibbs relation

$$d\varepsilon = T d\sigma + \mu d\rho + \mu_c dc + v_i dg_i + H_i dB_i + h_i^M dM_i$$
$$+ \Psi_{ij} du_{ij} \tag{1}$$

relating all macroscopically relevant variables discussed above to the entropy density σ. B is the magnetic induction field included here in order to accommodate the static Maxwell equations. In Eq. (1) the thermodynamic quantities, chemical potential μ, temperature T, relative chemical potential μ_c, velocity v_i, elastic stress Ψ_{ij}, magnetic field H_i, and the magnetic molecular field h_i^M, are defined as partial derivatives of the energy density with the respect to the appropriate variables [11].

To determine these thermodynamic forces and thus the static properties of magnetic elastomers one provides an expression of the energy density in terms of the variables

$$\varepsilon = \varepsilon_0 + \frac{B^2}{2} - \boldsymbol{B} \cdot \boldsymbol{M} + \frac{\mu_{ijkl}}{2} u_{ij} u_{kl} - \frac{\gamma_{ijkl}}{2} M_i M_j u_{kl} + \frac{\alpha}{2} M_i^2$$

$$+ \frac{\beta}{4}(M_i^2)^2 + u_{ii}(\chi^\rho \delta\rho + \chi^\sigma \delta\sigma + \chi^c \delta c), \tag{2}$$

where ε_0 is the energy density of a fluid binary mixture. Equation (2) explicitly contains the elastic and the magnetic energy, their cross coupling (the magnetoelastic energy) and bilinear couplings of compression with the scalar variables. To discuss large elastic deformations (rubber elasticity) one should keep terms of higher order of u_{ij}, which are ne-

glected here. The magnetoelastic coupling is cubic [12] and the M^4 contribution is kept in order to guarantee the thermodynamic stability. The tensors μ_{ijkl} and γ_{ijkl} take the isotropic form $a_{ijkl} = a_1 \delta_{ij}\delta_{kl} + a_2(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl})$, where μ_1 is the compressibility and μ_2 the shear modulus. The magnetoelastic energy is similar to that for ferromagnetic materials, where, however, the compressional magnetostriction is neglected ($\gamma_1 = 0$) [12]. We will not take this approximation for magnetic gels and keep $\gamma_1 \neq 0$, in order to explore effects due to a nonzero γ_1 and how they can be measured. While γ_1 describes the elastic response to changing the field strength (or vice versa compression or dilation due to changes in $|M|$), γ_2 is related to elastic shear and to rotations of M. Depending on how the "attachment" of the magnetic clusters to the network actually is realized in a sample, this interaction may be large or small. Thus measuring γ's by their effects described below, may give some hints on the microscopic structures. All static susceptibilities, such as the elastic and magnetoelastic moduli as well as those describing cross couplings between compression and the density, entropy density, and concentrations variations (χ^ρ, χ^σ, and χ^c, respectively) can depend on M^2 and thus on magnetic-field strength.

Using Eqs. (1) and (2), the magnetic Maxwell field H_i is defined in the usual way

$$H_i = \left(\frac{\partial\varepsilon}{\partial B_i}\right)_{M, u_{ij}, \ldots} = B_i - M_i, \tag{3}$$

while the magnetic molecular field h_i^M reads

$$h_i^M = \left(\frac{\partial\varepsilon}{\partial M_i}\right)_{B, u_{ij}, \ldots} = -B_i - \gamma_{ijkl} M_j u_{kl} + \alpha M_i + \beta M^2 M_i. \tag{4}$$

Note that because of definition (3), it is not possible to have a direct coupling between the external field $\boldsymbol{B}$ and the strain; the deformation of the network is mediated by the magnetization via the coupling terms $\sim \gamma_{ijkl}$.

The elastic stress Ψ_{ij} has the following form:

$$\Psi_{ij} = \left(\frac{\partial\varepsilon}{\partial u_{ij}}\right)_{M, B, \ldots}$$

$$= \mu_{ijkl} u_{kl} - \frac{\gamma_{ijkl}}{2} M_k M_l + \delta_{ij}(\chi^\rho \delta\rho + \chi^\sigma \delta\sigma + \chi^c \delta c) \tag{5}$$

and depends on the magnetization.

III. EQUILIBRIUM

In equilibrium, both the elastic strain Eq. (5) and the magnetic molecular field Eq. (4) have to be zero. Without an external field or external strain there is no magnetization and no strain in equilibrium. A finite external field, taken along the z axis, $\boldsymbol{B} = B_0 \boldsymbol{e}_z$, induces an equilibrium magnetization ($M^0 = M_0 \boldsymbol{e}_z$) and a nonzero strain u_{ij}^0 due to the magneto-

striction effect. Neglecting the couplings of density [18], entropy, and concentration to the strain tensor, we have

$$\Psi_{ij} = \left[\left(\mu_1 - \frac{2}{3}\mu_2 \right) u_{kk}^0 - \left(\frac{\gamma_1}{2} - \frac{\gamma_2}{3} \right) M_0^2 \right] \delta_{ij} - \gamma_2 M_i^0 M_j^0$$
$$+ 2\mu_2 u_{ij}^0 = 0, \tag{6}$$

$$h_i^M = -B_0 \delta_{iz} - \left(\gamma_1 - \frac{2}{3}\gamma_2 \right) M_i^0 u_{kk}^0 - 2\gamma_2 M_j^0 u_{ij}^0 + \alpha M_i^0$$
$$+ \beta M_0^2 M_i^0 = 0. \tag{7}$$

From $h_x^M = 0$, $h_y^M = 0$, and $\Psi_{xy} = 0$ it follows that $u_{xz}^0 = 0$, $u_{yz}^0 = 0$, and $u_{xy}^0 = 0$ accordingly. The remaining conditions give

$$u_{xx}^0 = u_{yy}^0 = \frac{\mu_2 \gamma_1 - \mu_1 \gamma_2}{6\mu_1 \mu_2} M_0^2, \tag{8}$$

$$u_{zz}^0 = \frac{\mu_2 \gamma_1 + 2\mu_1 \gamma_2}{6\mu_1 \mu_2} M_0^2, \tag{9}$$

leading to the volume change $U^0 \equiv u_{xx}^0 + u_{yy}^0 + u_{zz}^0 = (\gamma_1/2\mu_1)M_0^2$. The magnetostrictive volume change of the ferrogel is determined by the bulk modulus μ_1 and by the coefficient γ_1, which couples the trace of the stress tensor to the magnitude of the magnetization.

From $h_z^M = 0$ we get implicitly the equilibrium magnetization as a function of the field $B_0 = M_0[\alpha + \beta M_0^2 - (3\gamma_1^2 \mu_2 + 4\gamma_2^2 \mu_1)M_0^2/(6\mu_1\mu_2)]$. Writing this relation in the form $\chi B_0 = (1+\chi)M_0$, a field-dependent magnetic susceptibility χ results with

$$\frac{1+\chi}{\chi} = \alpha + \left(\beta - \frac{3\gamma_1^2 \mu_2 + 4\gamma_2^2 \mu_1}{6\mu_1\mu_2} \right) \left(\frac{\chi B_0}{1+\chi} \right)^2. \tag{10}$$

The explicit form of Eq. (10) follows from the (truncated) expansion (2) and is suitable for small external fields only. For high field intensities, when the magnetization reaches its saturation value, χ in Eq. (10) has to be replaced by a more complicated function $\chi_0 = \chi(B_0)$, either measured [13,14] or calculated from reliable microscopic models. For the small deviations from equilibrium, which we are dealing with in the following, the simple form $\chi B_0 = M_0$ is sufficient for any field strength, when for χ the appropriate equilibrium value χ_0 is taken.

Magnetostriction is a well-known phenomenon in single- or polycrystalline ferromagnetic solids [19]. A complicated interaction between the crystalline and domain structure with the magnetic moments of the atoms leads to a connection between elasticity and magnetic moment, e.g., to a change of volume or shape at the paramagnetic to ferromagnetic phase transition. Ferrogels, however, are isotropic and nonmagnetic without an external magnetic field. Magnetostriction is then a nonlinear effect. Applying a field, on the other hand, the induced magnetostriction can be considerably large due to the superparamagnetic response and the soft rubber elasticity. The induced deformations, Eqs. (8) and (9), are of uniaxial

symmetry and in this state the ferrogel behaves more like a uniaxial ferromagnet than an isotropic one.

IV. DYNAMICS

The hydrodynamic equations for conserved and slowly relaxing variables as well as for those associated with spontaneously broken continuous symmetries are

$$\frac{\partial}{\partial t}\rho + \mathrm{div}\,\rho\boldsymbol{v} = 0, \tag{11}$$

$$\frac{\partial}{\partial t}\sigma + \mathrm{div}\,\sigma\boldsymbol{v} + \mathrm{div}\,\boldsymbol{j}^\sigma = \frac{R}{T}, \tag{12}$$

$$\frac{\partial}{\partial t}g_i + \boldsymbol{\nabla}_j(v_j g_i + \delta_{ij}[p_0 + \boldsymbol{B}\cdot\boldsymbol{H}] + \sigma_{ij}^{th} + \sigma_{ij}) = 0, \tag{13}$$

$$\left(\frac{\partial}{\partial t} + v_k \boldsymbol{\nabla}_k \right) u_{ij} + Y_{ij} = 0, \tag{14}$$

$$\rho \left(\frac{\partial}{\partial t} + v_j \boldsymbol{\nabla}_j \right) c + \mathrm{div}\,\boldsymbol{j}^c = 0, \tag{15}$$

$$\left(\frac{\partial}{\partial t} + v_j \boldsymbol{\nabla}_j \right) M_i + (\boldsymbol{M} \times \boldsymbol{\omega})_i + X_i = 0, \tag{16}$$

where $\omega_i = \frac{1}{2}\epsilon_{ijk}\boldsymbol{\nabla}_j v_k$ is the vorticity and

$$\sigma_{ij}^{th} = -B_j H_i - \frac{1}{2}(M_j h_i^M - M_i h_j^M) + \Psi_{jk} u_{ki}. \tag{17}$$

Using the fact that the energy density, Eq. (1), has to be invariant under constant rotation [11], Eq. (17) can be simplified as

$$\sigma_{ij}^{th} = -\frac{1}{2}(B_i H_j + B_j H_i) + \frac{1}{2}(\Psi_{jk} u_{ki} + \Psi_{ik} u_{kj}). \tag{18}$$

The last term in Eq. (18) is nonlinear, but since there is a finite strain in an external field, it will enter linear deviations from that constrained equilibrium. The thermodynamic pressure p_0's given by

$$p_0 = -\varepsilon + T\sigma + \mu\rho + \mathbf{g}\cdot\mathbf{v}. \tag{19}$$

j^σ is the entropy current, in Eqs. (14)–(16) Y_{ij} and X_i are the quasicurrents of the variables associated with broken translational symmetry (network) and slowly relaxing magnetization. To guarantee rotational invariance of the dynamical equation for the strain field, one must require $Y_{ij} = Y_{ji}$. The source term R/T in the dynamic equation for the entropy density is the entropy production. The second law of thermodynamics reads $R \geq 0$ for dissipative and reversible process, respectively.

Since we are not dealing with electromagnetic effects, we can use the static Maxwell equations to determine $\boldsymbol{B}$

$$\mathrm{curl}\,\boldsymbol{H} = \mathrm{curl}(\boldsymbol{B} - \boldsymbol{M}) = 0, \quad \mathrm{div}\,\boldsymbol{B} = 0. \tag{20}$$

All the currents can be split into dissipative and into reversible ($R = 0$) and irreversible ($R \geq 0$) parts. Using general

symmetry and invariance arguments and the fact that a magnetic field changes sign under time reversal, we obtain the linear currents

$$j_i^{\sigma R} = -\kappa_{ij}^R(M)\nabla_j T - D_{ij}^{TR}(M)\nabla_j\mu_c + \xi_{ij}^{TR}(M)\Psi_j, \tag{21}$$

$$j_i^{cR} = -D_{ij}^R(M)\nabla_j\mu_c + D_{ij}^{TR}(M)\nabla_j T + \xi_{ij}^{cR}(M)\Psi_j, \tag{22}$$

$$\sigma_{ij}^R = -\Psi_{ij} - c_{kij}^R(M)h_k^M - \nu_{ijkl}^R(M)A_{kl}, \tag{23}$$

$$Y_{ij}^R = -A_{ij} + \tfrac{1}{2}\lambda^M[\nabla_i(\nabla\times\boldsymbol{h}^M)_j + \nabla_j(\nabla\times\boldsymbol{h}^M)_i]$$
$$-\tfrac{1}{2}[\nabla_i\{\xi_{jk}^R(M)\Psi_k + \xi_{jk}^{TR}(M)\nabla_k T + \xi_{jk}^{cR}(M)\nabla_k\mu_c\}$$
$$+(i\leftrightarrow j)], \tag{24}$$

$$X_i^R = b_{ij}^R(M)h_j^M + \lambda^M(\nabla\times\boldsymbol{\Psi})_i - c_{ijk}^R(M)A_{jk}, \tag{25}$$

with $A_{ij}=\tfrac{1}{2}(\nabla_i v_j+\nabla_j v_i)$ and $\Psi_i=\nabla_j\Psi_{ij}=\nabla_j\Psi_{ji}$. Again, nonlinear elastic contributions have been neglected. Due to the new degree of freedom (magnetization) there is an additional term in the stress quasicurrent, Eq. (24), and a counter term in X_i^R, which describes a dynamic cross coupling between magnetization and the network. It does not exist in ordinary elastomers nor in isotropic ferrofluids. Its impact on the sound spectrum will be explored in Sec. V B. The new coefficient λ^M (reversible dynamic coupling between the magnetization and the strain tensor) gives a small effect in the dynamics of order $\sim k^4$. The magnetization-dependent tensors $\kappa_{ij}^R(M)$, $D_{ij}^R(M)$, $D_{ij}^{TR}(M)$, $\nu_{ijkl}^R(M)$, $c_{ijk}^R(M)$, $\xi_{ij}^{TR}(M)$, $\xi_{ij}^{cR}(M)$, $\xi_{ij}^R(M)$, $b_{ij}^R(M)$ are all odd functions of the magnetization and are listed to linear order in M_0 in the Appendix.

To derive the dissipative contributions to the currents it is most convenient to start with the expression for dissipation function R. The dissipative currents are then obtained by taking variational derivatives with respect to one thermodynamic conjugate while keeping all others fixed. Expanding the dissipation function R up to second order in the thermodynamic forces we obtain

$$R = \frac{1}{2}\kappa(\nabla_i T)^2 + \frac{1}{2}\nu_{ijkl}A_{ij}A_{kl} + \frac{1}{2}D(\nabla_i\mu_c)^2 + \frac{b}{2}(h_i^M)^2$$

$$+\frac{1}{2}\xi(\Psi_i)^2 + D^T(\nabla_j T)(\nabla_j\mu_c)$$

$$+\Psi_i(\xi^T\nabla_i T + \xi^c\nabla_i\mu_c). \tag{26}$$

Here ν_{ijkl} is the viscosity tensor and κ, D, and D^T describe heat conduction, diffusion, and thermodiffusion, respectively. The quantity b is the inverse magnetization relaxation and ξ the self-diffusion constant of the strain field. The range of possible values of the coefficients in Eq. (26) is restricted by the positivity of the entropy production.

We derive the dissipative parts of the currents by taking the variational derivative of the dissipation function with respect to the appropriate thermodynamic force

$$j_i^{\sigma D} = -\kappa\nabla_i T - D^T\nabla_i\mu_c - \tfrac{1}{2}\xi^T\Psi_i, \tag{27}$$

$$j_i^{cD} = -D\nabla_i\mu_c - D^T\nabla_i T - \tfrac{1}{2}\xi^c\Psi_i, \tag{28}$$

$$\sigma_{ij}^D = -\nu_{ijkl}A_{kl}, \tag{29}$$

$$Y_{ij}^D = -\tfrac{1}{2}[\nabla_i(\xi\Psi_j + \xi^T\nabla_j T + \xi^c\nabla_j\mu_c) + (i\leftrightarrow j)], \tag{30}$$

$$X_i^D = bh_i^M. \tag{31}$$

V. EXPERIMENTS

A. Static elongation and shear

In preparation for, and for comparison with, the sound spectrum we first discuss static elongational and shear deformations. We assume an external field (along the z axis) that gives a nonzero magnetization as well as a deformation in equilibrium. This state is then disturbed by an external deformation Δu_{ij} by some mechanical device. Due to the magnetostriction effect this gives also rise to a change in the magnetization. In the static limit the magnetic degree of freedom is still in equilibrium and the change of the magnetization can be obtained from the condition $h_i^M=0$, Eq. (4). The applied deformation gives, directly by Hooke's law and indirectly by the change of the magnetization, an elastic stress. From Eq. (5) we get

$$\Psi_{zz} = (\mu'' - \chi_0\gamma''^2 M_0^2)\Delta u_{zz}$$
$$+ (\mu' - \chi_0\gamma'\gamma''M_0^2)(\Delta u_{xx}+\Delta u_{yy}), \tag{32}$$

$$\Psi_{xx} = (\mu'' - \chi_0\gamma'^2 M_0^2)\Delta u_{xx} + (\mu' - \chi_0\gamma'^2 M_0^2)\Delta u_{yy}$$
$$+ (\mu' - \chi_0\gamma'\gamma''M_0^2)\Delta u_{zz}, \tag{33}$$

$$\Psi_{zx} = 2(\mu_2 - \chi_0\gamma_2^2 M_0^2)\Delta u_{zx}, \tag{34}$$

$$\Psi_{xy} = 2\mu_2\Delta u_{xy} \tag{35}$$

for the elastic stresses. Apart from the elastic moduli [$\mu'' = \mu_1 + (4/3)\mu_2$ and $\mu' = \mu_1 - (2/3)\mu_2$], it contains M_0^2 corrections due to magnetostriction [$\gamma' = \gamma_1 - (2/3)\gamma_2$ and $\gamma'' = \gamma_1 + (4/3)\gamma_2$], except for deformations that do not affect the magnetization. Note that, even if the deformation does conserve the volume ($\Delta u_{xx} + \Delta u_{yy} + \Delta u_{zz}=0$), the trace of the elastic stress tensor is not zero, but given by $\Psi_{kk} = -6\chi_0\gamma_1\gamma_2 M_0^2\Delta u_{zz}$. Formulas (32)–(35) are applicable for small strains only, since it is based on Hooke's law, while for larger strains deviations from this law due to rubber elasticity are to be expected.

The stress tensor σ_{ij} not only contains the elastic stress Ψ_{ij}, but also the hydrostatic pressure and a nonlinear combination of elastic stress and strain, Eq. (18). The former couples to volume deformations via the compressibility κ_s, defined as $\kappa_s = \rho^2(\partial^2\varepsilon/\partial\rho^2)^{-1}$. The latter gives rise to linear contributions in the stress tensor, if an external field is present, since then a finite deformation (strain) is induced. This is seen in the sound spectrum discussed below.

B. Propagation of sound

Due to the presence of the permanent polymer network in ferrogels compared to ferrofluids, there are transverse as well as longitudinal sound eigenmodes. In this section we derive the longitudinal and the transverse sound of the system with an external magnetic field parallel to the z axis. We neglect all diffusional processes connected, e.g., with viscosity and heat conduction as well as their reversible counterparts. Terms with λ and b^R coefficients are omitted here as well. The first one does not contribute to the sound velocity, because it is of fourth order in the wave vector $\sim k$. Terms with b^R shift the magnetization relaxation time by $\sim b^R M^2$, and thus give higher order corrections $\sim M^4$ to the sound spectrum, in which we are not interested here. Only the relaxation of the magnetization in the field is kept.

Assuming a one-dimensional plane wave with space-time dependence $\sim \exp i(-\omega t + \mathbf{k} \cdot \mathbf{r})$ for all deviations δu_{ij}, δM_i, v_i, $\delta\rho$ from the equilibrium values determined in Sec. III the linearized set of dynamic equations becomes an algebraic one. Let us consider sound in the two cases, where the external magnetic field and the equilibrium magnetization are either perpendicular or parallel to the wave vector. Field fluctuations δB_i are fixed by the static Maxwell equations (20) to $\delta B_i = \delta M_j(\delta_{ij} - k_i k_j k^{-2})$.

In the case where an external field is perpendicular to the wave vector the sound dispersion relations for longitudinal and for transverse modes, respectively, read, up to order $O(M^2)$ from here on all old μ' are called $\tilde{\mu}$

$$\omega_l^2 = \frac{k^2}{\rho}\left[\tilde{\mu} - M_0^2\left(\tilde{\mu}\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\mu_2\mu_1} + \chi_0(\gamma')^2 \right.\right.$$
$$\left.\left. - \frac{\iota\omega(\chi_0\gamma' - c_2^R)^2}{\iota\omega\chi_0 - b}\right)\right], \tag{36}$$

$$\omega_{t1}^2 = \frac{k^2}{\rho}\left[\mu_2 - M_0^2\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\mu_1}\right], \tag{37}$$

$$\omega_{t2}^2 = \frac{k^2}{\rho}\left[\mu_2 - M_0^2\left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\mu_1} + \chi_0\gamma_2^2 + \frac{\gamma_2}{2}\right.\right.$$
$$\left.\left. - \frac{\iota\omega(\chi_0\gamma_2 - c_1^R + \frac{1}{2})^2}{\iota\omega\chi_0 - b}\right)\right], \tag{38}$$

where $\tilde{\mu} = 1/(\rho\kappa_s) + \mu_1 + \frac{4}{3}\mu_2$ and $\gamma' = \gamma_1 - \frac{2}{3}\gamma_2$. Generally, $\chi_0(B_0)$ brings in an additional dependence on M_0, which however can be neglected in $O(M^2)$.

If an external field is parallel to the wave vector we have the following longitudinal and transverse dispersion relations:

$$\omega_l^2 = \frac{k^2}{\rho}\left[\tilde{\mu} - M_0^2\left(\tilde{\mu}\frac{\mu_2\gamma_1 + 2\mu_1\gamma_2}{6\mu_2\mu_1} + \chi_0(\gamma'')^2 \right.\right.$$
$$\left.\left. - \frac{\iota\omega[\chi_0\gamma'' - (2c_1^R + c_2^R)]^2}{\iota\omega\chi_0 - b}\right)\right], \tag{39}$$

$$\omega_t^2 = \frac{k^2}{\rho}\left[\mu_2 - M_0^2\left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\mu_1} + \chi_0\gamma_2^2 - \frac{\gamma_2}{2}\right.\right.$$
$$\left.\left. - \frac{\iota\omega(\chi_0\gamma_2 - c_1^R - \frac{1}{2})^2}{\iota\omega\chi_0 - b}\right)\right], \tag{40}$$

where $\gamma'' = \gamma_1 + \frac{4}{3}\gamma_2$. As the problem is symmetric in the plane perpendicular to the magnetic field the two transverse sounds have identical dispersion relations.

Knowing the dispersion relations for the two geometries one can study sound velocities. The relaxation time of the magnetization $\tau_M = \chi_0/b$ is known for ferrofluids and is typically of order 10^{-4}. Our approach allows us to investigate two frequency regimes: for $\omega < 1/\tau_M$ the low frequency limit and for $\omega > 1/\tau_M$ the high frequency regime. There is no frequency dependence for the transverse sound mode, where the magnetic field, the wave vector, and the velocity are mutually perpendicular, Eq. (37).

Let us first investigate low frequencies ($\omega < 1/\tau_M$). The frequency-dependent parts in the square brackets of the dispersion relations (36)–(40) become dissipative and do not contribute to the sound velocities. In the case of the external field being perpendicular to the wave vector the velocities of the longitudinal c_l and the transverse sounds c_{t1}, c_{t2} read

$$c_l^2 = \frac{\tilde{\mu}}{\rho} - \left(\tilde{\mu}\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\rho\mu_2\mu_1} + \frac{\chi_0(\gamma')^2}{\rho}\right)M_0^2, \tag{41}$$

$$c_{t1}^2 = \frac{\mu_2}{\rho} - \left(\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\rho\mu_1}\right)M_0^2, \tag{42}$$

$$c_{t2}^2 = \frac{\mu_2}{\rho} - \left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\rho\mu_1} + \frac{2\chi_0\gamma_2^2 + \gamma_2}{2\rho}\right)M_0^2, \tag{43}$$

while for a parallel field we have

$$c_l^2 = \frac{\tilde{\mu}}{\rho} - \left(\tilde{\mu}\frac{\mu_2\gamma_1 + 2\mu_1\gamma_2}{6\rho\mu_1\mu_2} + \frac{\chi_0(\gamma'')^2}{\rho}\right)M_0^2, \tag{44}$$

$$c_t^2 = \frac{\mu_2}{\rho} - \left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\rho\mu_1} + \frac{2\chi_0\gamma_2^2 - \gamma_2}{2\rho}\right)M_0^2. \tag{45}$$

The sound speeds at low frequencies and zero field give information about the compressibility and the elastic moduli (bulk and shear). The dependence on M_0^2 is due to magnetostrictive effect and completely absent for $\gamma_1 = 0 = \gamma_2$. Magnetostriction enters the sound speed in different ways. There is a direct static coupling of magnetization and stress in Eq. (5) and the strain dependence of the magnetic molecular field (4), which give rise to terms linear and quadratic in γ_1 and γ_2. A similar term emerges indirectly via the Maxwell stress. The second route is dynamic, given by the nonlinear elastic stress contribution to the stress tensor in Eq. (18), which, however, is effectively linear due to the nonzero equilibrium strains. In the sound speeds these contributions are of the bilinear $\gamma\mu$ type. In an external field the effective moduli measured by sound propagation are therefore different from

those given by the static elastic stress Ψ_{ij} discussed in the preceding section. The coincidence of static linear elasticity and low frequency sound speed is restored in the limit of vanishing magnetic field, when no magnetostrictive deformation is present and the additional contribution in the stress tensor σ_{ij} (18) is nonlinear and absent in the sound spectra. Of course, in this limit the sound spectra are isotropic as is the ferrogel.

The sound velocities change with an external magnetic field basically with the second power of the field, which is in accordance with experiments on longitudinal sound [14]. There is, however, an additional field dependence through χ_0. Whether the sound velocities are decreased or increased by the field cannot be established by general rules, since the signs of $\gamma_{1,2}$ are not fixed and can be material dependent. Measurements of transverse and longitudinal sound velocities in the different geometries will provide information on the magnitude and sign of the magnetostrictive and elastic moduli. As a first approximation the magnetostrictive volume change ($\sim \gamma_1 M_0^2/\mu_1$) can be neglected in those rubbers and only shape changes remain.

Damping of sound waves generally is rather weak and given by the imaginary part of the dispersion relation. In addition to the usual magnetic-field-independent sound damping due to viscosity and other diffusional processes there is a field-dependent sound damping in ferrogels. This is an effect of the reversible, dynamic coupling of the magnetization to flow, either phenomenological [$c_{ijk}^R(M)$ in Eq. (25)] or kinematic [$\epsilon_{ijk}M_j\omega_k$ in Eq. (16)] and its counterparts in the Navier-Stokes equation. For example, when the magnetic field is parallel (perpendicular) to the wave vector a field-dependent damping of longitudinal (transverse) sound Eq. (39) [Eq. (38)] reads, respectively,

$$\text{Im}(\omega_l) = -\frac{1}{2}\frac{[\chi_0\gamma'' - (2c_1^R + c_2^R)]^2}{\rho b}M_0^2 k^2, \qquad (46)$$

$$\text{Im}(\omega_{t2}) = -\frac{1}{2}\frac{(\chi_0\gamma_2 - c_1^R + \frac{1}{2})^2}{\rho b}M_0^2 k^2, \qquad (47)$$

the first of which can be related to the observed increase of the apparent viscosity due to the magnetic field [15]. In all cases $\text{Im} < 0$, as it should be according to the second law of thermodynamics.

Let us now investigate the high frequency limit for $\omega > 1/\tau_M$. In the case where an external field is perpendicular to the wave vector the velocities of the longitudinal c_l and the transverse sounds c_{t2} read (c_{t1} is as in the low frequency limit)

$$c_l^2 = \frac{\tilde{\mu}}{\rho} - \left(\tilde{\mu}\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\rho\mu_2\mu_1} + \frac{c_2^R(2\chi_0\gamma' - c_2^R)}{\chi_0\rho}\right)M_0^2, \quad (48)$$

$$c_{t2}^2 = \frac{\mu_2}{\rho} - \left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\rho\mu_1}\right.$$
$$\left. + \frac{2\chi_0\gamma_2(c_1^R - \frac{1}{4}) - (c_1^R - \frac{1}{2})^2}{\chi_0\rho}\right)M_0^2. \qquad (49)$$
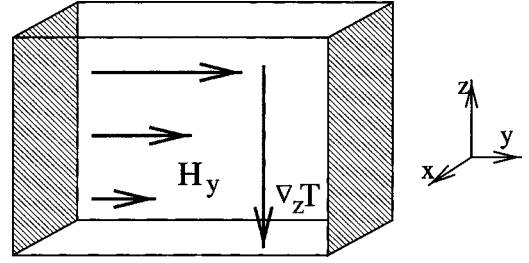

FIG. 1. Shear excitation u_{xz} in a ferrogel due to applied temperature oscillations along the z direction, in the presence of a constant or gradient magnetic field in y direction.

For an external field parallel to the wave vector we have

$$c_l^2 = \frac{\tilde{\mu}}{\rho} - \left(\tilde{\mu}\frac{\mu_2\gamma_1 + 2\mu_1\gamma_2}{6\mu_2\mu_1\rho}\right.$$
$$\left. + \frac{(2c_1^R + c_2^R)[2\chi_0\gamma'' - (2c_1^R + c_2^R)]}{\chi_0\rho}\right)M_0^2, \quad (50)$$

$$c_t^2 = \frac{\mu_2}{\rho} - \left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\mu_1\rho}\right.$$
$$\left. + \frac{2\chi_0\gamma_2\left(c_1^R + \frac{1}{4}\right) - \left(c_1^R + \frac{1}{2}\right)^2}{\chi_0\rho}\right)M_0^2. \qquad (51)$$

The field dependence of the sound velocities contains the magnetostrictive contributions already present in the low frequency limit, but in addition also the reversible, dynamic cross couplings (c_1^R, c_2^R) between magnetization and flow (which in the low frequency limit contributed to the sound damping). Of course, most interesting experimentally is the transition region $\omega\tau_M \approx 1$, where the sound velocities make steps and the damping is enhanced.

C. Shear excitation by temperature oscillations

In ferrogels there are several reversible cross couplings mediated by material tensors that are linear in the external magnetic field. They belong to the same type of effects as the Hall and the Righi-Leduc effect. In Eq. (24) there is such a coupling, described by $\xi_{jk}^{TR}(M)$, between a temperature gradient and the dynamics of the elastic degree of freedom. From the form of ξ_{ij}^{TR} (A1) one can conclude that an applied oscillating temperature $T = T_0 + T_1\exp[i(kz - \omega t)]$, in the presence of a homogeneous or gradient magnetic field [20] $H = \hat{e}_y(H_0 + H_1 z)$, leads to an oscillating shear in the plane perpendicular to the magnetic field (Fig. 1), since $Y_{xz} \sim a \equiv \frac{1}{2}\chi_0\xi^{TR}T_1(H_1 + ikH_0)$. Oscillating shear u_{xz} is part of the transverse sound discussed in the preceding section. After the initial transients have died out the excited shear wave travels with the frequency and wave vector of the applied temperature, $u_{xz} = u_0\exp[i(kz - \omega t)]$, with the complex amplitude u_0 given by

$$\left(-i\omega-\frac{c_{t1}^2 k^2}{i\omega-\frac{\nu}{\rho}k^2}+\xi\mu_2 k^2\right)u_0=ika, \qquad (52)$$

where c_{t1} is the shear wave velocity (42), ν the shear viscosity, and ξ the self-diffusion of the strain field (30). The former comprises of a field-dependent part, which is space dependent in a gradient field. However, that part is small compared to the constant one (μ_2/ρ) and can be approximated by its spatial mean or can be neglected at all here. If the ratio ω/k for the applied temperature is in the range of the transverse sound velocity, we have $\omega\gg(\nu/\rho)k^2$ and $\omega\gg\xi\mu_2 k^2$, and Eq. (52) gives the amplitude of the excited shear wave in the long time limit in the form of a response of a damped harmonic oscillator

$$u_0=\frac{-ak\omega}{\omega_0^2-\omega^2+2i\omega\Gamma}, \qquad (53)$$

with eigenfrequency $\omega_0=c_{t1}k$ and damping $2\Gamma=k^2(\xi\mu_2+\nu/\rho)$.

The real part of the strain tensor, which is the measurable quantity, has the form

$$\mathrm{Re}(u_{xz})=A_{1,2}\cos(kz-\omega t+\delta_{1,2}), \qquad (54)$$

where $A_{1,2}=a_{1,2}k\omega[(\omega_0^2-\omega^2)^2+4\omega^2\Gamma^2]^{-1/2}$ and $\delta_2=\delta$, $\delta_1=\delta-\pi/2$ with $\tan\delta=(\omega^2-\omega_0^2)/(2\omega\Gamma)$ for the two cases of a constant magnetic field $a_2=\frac{1}{2}\chi_0\xi^{TR}T_1kH_0$ and a field gradient $a_1=\frac{1}{2}\chi_0\xi^{TR}T_1H_1$, respectively. This reduces to

$$u_{xz}=\frac{a_1 k}{2\Gamma}\sin(kz-\omega_0 t) \quad \text{or} \quad u_{xz}=\frac{a_2 k}{2\Gamma}\cos(kz-\omega_0 t) \qquad (55)$$

in the resonant cases $\omega=\omega_0$. Of course, this coupling of temperature to shear also works the other way round, and an imposed shear wave can excite a temperature wave in the presence of an appropriate magnetic field (gradient).

Another possibility of shear excitation is the application of concentration instead of a temperature oscillations [see Eq. (24)], although this might be more challenging experimentally.

VI. CONCLUSION

In this paper we have given the hydrodynamic equations for magnetic elastomers including the magnetization as an independent slowly relaxing variable, which allows us to study the system for high frequencies as well. Due to presence of the permanent network the displacement field **u** turns out to be a truly hydrodynamic variable. The fact that magnetic grains are attached to the network is expressed by the static coupling of the magnetization and the strain tensor. This leads to an additional field-dependent contribution to

the sound spectrum. The contribution to the transverse sound modes depends on the relative angle between an external field and the wave vector. From the low frequency limit of the sound spectrum one can obtain information about the effective, magnetic-field-dependent elastic moduli. However, these moduli are different from those measured by static elongations or shear deformations in an external field. The reason is that due to the finite magnetostriction the linear response theory is not applicable. Only in the limit of a vanishing field are they equal and match the true elastic moduli. In the high frequency limit one gets a shift in the sound velocities proportional to the dynamic coupling between the flow and the magnetization. This reflects the fact that the magnetization is an independent variable. Finally, a shear excitation experiment in an oscillating temperature gradient plus a gradient of the magnetic field has been proposed.

APPENDIX: TENSORS LINEAR IN M

Here we give the form of those tensors that do not exist without a magnetic field and change sign when the magnetization changes sign. For simplicity, we restrict ourselves to the case linear in M. The reversible second-rank magnetization-dependent material tensors, such as the reversible analog of heat conduction $\kappa_{ij}^R(M)$, diffusion $D_{ij}^R(M)$, thermodiffusion $D_{ij}^{TR}(M)$, magnetization relaxation $b_{ij}^R(M)$, and the reversible coupling terms between temperature, concentration, and elasticity, ξ_{ij}^{TR}, ξ_{ij}^{cR}, ξ_{ij}^R, are all of the form

$$\kappa_{ij}^R(M)=\kappa^R\epsilon_{ijk}M_k. \qquad (A1)$$

They are antisymmetric $\kappa_{ij}^R(M)=-\kappa_{ji}^R(M)$ according to Onsager's relation $\kappa_{ij}^R(M)=\kappa_{ji}^R(-M)$ and give zero entropy production [17].

The third-rank tensor c_{ijk}^R describing a reversible dynamic cross coupling between flow and magnetization is symmetric in the two last indices and reads

$$c_{ijk}^R(M)=c_1^R(\delta_{ij}M_k+\delta_{ik}M_j)+c_2^R\delta_{jk}M_i. \qquad (A2)$$

The reversible analog of the viscosity tensor has one component for the isotropic case [17]

$$\nu_{ijkl}^R(M)=\nu^R[\epsilon_{ikp}\delta_{jl}+\epsilon_{ilp}\delta_{jk}+\epsilon_{jlp}\delta_{ik}+\epsilon_{jkp}\delta_{il}]M_p. \qquad (A3)$$

This fourth-order tensor is symmetric in i,j and in k,l, but is antisymmetric under the exchange of the first pair of indices with the second one, thus guaranteeing zero entropy production.

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