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ORIGINAL CONTRIBUTION

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Semiclassical approach to electrorheological fluids. Influence of solid volume fraction on the suspension yield stress

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Abstract A semiclassical approach, previously proposed in matter and momentum transport phenomena, has been employed to deal with the electrorheological effect. The vibrational Helmholtz free energy of a solidlike medium, consisting of phononic and dielectric contributions, has been developed in terms of Debye, optical and characteristic system frequencies and constrained to a stationary condition with respect to mass-density variations. It turns out that application of an electric field results in the creation of bound energy states, which can be related to the solid fraction and the yield stress through a phenomenological equation. Application to rheological data, from polyaniline particles and chlorinated paraffin in silicon oil, silica spheres in corn oil and numerical simulations, is presented.

Keywords Electrorheological fluids · Semiclassical physics · Collective quasi-particle mechanisms · Solid volume fraction · Suspension yield stress

Introduction and account of previous work

In previous work [1], the isothermal sintering of a solid body was investigated starting from the state equation of the phonon gas in the Debye approximation (i.e., the free energy, F_0) [2]. Matter transport was described by a semiclassical equation, for the mass density as a function of time, which involves the Debye frequency, a Gruneisen parameter and a new characteristic temperature, accounting for the diffusion coefficient and the surface tension at the grain boundary. The same procedure was subsequently applied to describe momentum transport in thixotropic fluids, whose apparent viscosity is a function of the rate of shear applied [3]. We achieved a law conceptually equivalent to a sintering equation, where the Gruneisen parameter was redefined with respect to viscosity variations and another characteristic Debye-like temperature took into account the time scale of the diffusional mechanism in the bulk phase. In Refs. [1–3], we introduced a restriction to the Helmholtz energy ($F_{\Omega 0}$) by weighting the density of vibrational modes (σ) with one element of a δ-convergent sequence of ordinary functions ($\delta_{\tilde{\varepsilon}}$) [4]:

$$F_{\Omega 0} = -\int \ln(1 - e^{-\hbar\beta\omega})\psi_{\tilde{\varepsilon}}(\omega, \Omega)d\omega + \text{constant} \ , \quad (1)$$

where ω is the frequency, $\hbar$ is the Planck constant, $\beta = 1/(k_B T)$ is the inverse of the Boltzmann constant, k_B, times the absolute temperature, T, and

$$\psi_{\tilde{\varepsilon}}(\omega, \Omega) = v\sigma(\omega)\delta_{\tilde{\varepsilon}}(\Omega) \ . \quad (2)$$

In the last relation, v normalizes the Dirac contribution to some net distribution area (conventional, and dimensioned to a frequency), while

$$\delta_{\tilde{\varepsilon}}(\omega, \Omega) = \frac{1}{\pi}\frac{\tilde{\varepsilon}}{\tilde{\varepsilon}^2 + \Omega^2} \ , \quad (3)$$

with $\lim_{\tilde{\varepsilon}\to 0}\delta_{\tilde{\varepsilon}} = \delta(\omega_c)$. The displacement $\Omega = \omega - \omega_c$ refers to some characteristic frequency value ω_c and $\tilde{\varepsilon}$ to the distribution variance, related to the microstructural disorder. The integral in Eq. (1) admits a rather simple approximation in the limit $\frac{\tilde{\varepsilon}}{(\omega_c)} \ll 1$ [1]:

$$F_{\Omega 0} \simeq -\frac{\sigma_{0v}\omega_c^2}{\pi\tilde{\varepsilon}}\Omega_d[\hbar\beta\Omega_d + \ln(1 - e^{-\hbar\beta\omega_d}) - 1] + \text{constant} \ , \tag{4}$$

where $\Omega_d = \omega_d – \omega_c$, ω_d is the effective Debye frequency and σ_{0v} is a constant term, proportional to the volume, v, (say, $\sigma_0 v \simeq \sigma_{0v} v$). Matter and momentum transport were investigated upon application to Eq. (4) of a general steady-state condition, with respect to time and the set of basic quantities implied. In this work, the previously described approach is further extended in order to deal with the electrorheological (ER) effect, namely, the dramatic change of rheological properties caused by the application of moderately high electric fields [5]. Generally, it occurs in dispersions of solid particles in dielectric or elastomeric media and in special polymeric systems, and is accompanied by the formation of percolating columnar fibers [6]. More precisely [7], for weak electric fields ER fluids exhibit ordering only in the field direction. For weak thermal fluctuations, the largely body centered cubic ordering changes into tetragonal order under the influence of an electric field. For field strengths sufficiently large compared to thermal fluctuations, ER suspensions become glassylike with columns without further meaningful ordering. Influence of the electric field strength, $\bar{E}$, on apparent viscosity and yield stress have been extensively studied, both experimentally and theoretically [5, 8–12]. Here, we restrict ourselves to the yield stress, τ_0, as a function of the solid volume fraction, ϕ. In dispersions of interacting units and hard spheres, the influence of the suspended fraction on rheology has been extensively examined [13, 14]. In this case, yield stress in ER fluids, either static or dynamic, is always connected to the electrostatic dispersion energy, the strength of which is commonly proportional to $\bar{E}^2$ (but deviations can be observed at high and low $\bar{E}$ values) [15]. Concerning the effect of the solid fraction, polarization and conduction theories predict the yield stress should ideally be proportional to ϕ [16]. Nevertheless, in dilute and highly concentrated regimes, the experimental slope of $\tau_0 = \tau_0(\phi)$ frequently differs from unity, and is greater than 1 for intermediate ϕ values [17]. Here, the semiclassical law proposed can account for the dependence of τ_0 versus ϕ in a wide enough volume fraction range.

Theory

According to the laws of thermodynamics and electromagnetic theory, the Helmholtz free energy, F, of a material with dielectric constant ε, kept at constant temperature and subject to an electric field, E, is [18]

$$F(T,E) = F_0(T) + F_\varepsilon(E) \ , \tag{5}$$

where if $\mathrm{d}v$ denotes the infinitesimal sample volume, we have [19]

$$F_\varepsilon = \frac{1}{2}\int \varepsilon E^2 \mathrm{d}v \ . \tag{6}$$

Following Eqs. (1), (2) and (3) and defining

$$F_{\Omega\varepsilon} = \frac{1}{\omega_1}\int F_\varepsilon \, \mathrm{d}\omega \tag{7}$$

we evaluate

$$F_\Omega = F_{\Omega 0} + F_{\Omega\varepsilon} \ , \tag{8}$$

where the first contribution on the right is still given by Eq. (4), and with

$$F_{\Omega\varepsilon} = \frac{1}{2\omega_1}\iint \delta_{\tilde{\varepsilon}}(\Omega)\varepsilon(\omega)E^2(\omega, v)\mathrm{d}v\mathrm{d}\omega \ . \tag{9}$$

To proceed, consider a static and spatially averaged electric field, $E(\omega, v) \simeq \bar{E}$, and, in all generality, the frequency dependence for the dielectric constant of an ionic crystal [20]:

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\omega_l^2 - \omega^2}{\omega_t^2 - \omega^2} \ . \tag{10}$$

This leads to the so-called Lyddane–Sachs–Teller (LST) relation [20]:

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \frac{\omega_l^2}{\omega_t^2} \ , \tag{11}$$

ω_l, ω_t, ε_0 and ε_∞ being the longitudinal and transverse optical phonon frequencies and the static and optical dielectric constants, respectively. Equation (10) can be derived by coupling the electric field, $\bar{E}$, of photons with the dielectric polarization of transverse optical phonons, giving rise to a quasi-particle concept termed polariton. Typical orders of magnitudes are $\omega_{t,l} \simeq (1 - 25) \times 10^{13}\mathrm{s}^{-1}$, $\varepsilon \simeq 5 - 30$ and $\varepsilon_\infty \simeq 1 - 15$. Equations (4), (5), (6), (7), (8), (9) and (10), namely, the frequency spectra involved, are summarized in Fig. 1. We can recognize the density of vibrational modes in the Debye approximation (Eq. 4), the contribution peaked at the characteristic frequency (see Eq. 3), and the spectrum for the dielectric constant, modeled in terms of the LST relation (Eq. 9). To take separately into account the effect of each characteristic term, the phononic contribution in Eq. (1) is still evaluated up to the Debye frequency, whereas we approximate Eq. (9) at the longitudinal optical phonon frequency (Fig. 1). Moreover, we assume $\tilde{\varepsilon} \ll \omega_c \ll \omega_{d,l,t}$ [1, 3], large enough temperature values and, for both ionic and nonionic media, get in the end (see Appendix)

$$F_\Omega \simeq -\frac{\sigma_{0v}\omega_d\omega_c^2}{\pi\tilde{\varepsilon}} \ln(\hbar\beta\omega_d) + \frac{v\varepsilon_0\bar{E}^2 v}{4\omega_1} + \text{constant} \ . \tag{12}$$

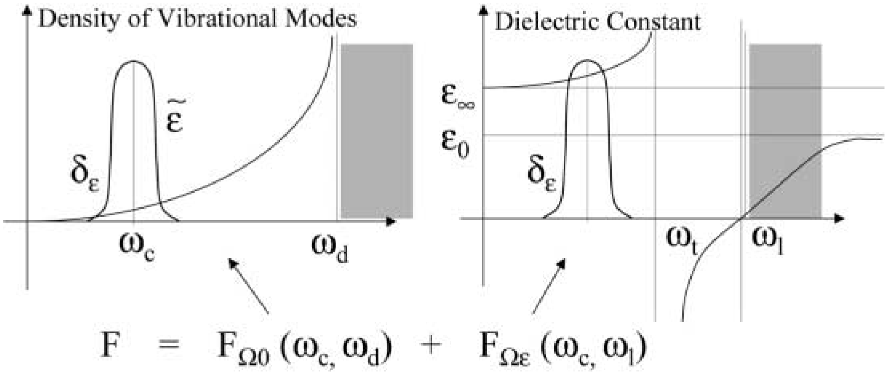

Fig. 1 Scheme of the Debye-like approximation employed and the frequency spectra involved

Consider now the contribution coming from the particles aligned by the field. In the columnar volume where they are confined [21], we can identify a subdispersion that, when $E = 0 \to \bar{E} \neq 0$, increases its density until a stationary energy state (Fig. 2):

$$\left(\frac{\partial F_\Omega}{\partial \rho}\right)_{T,\bar{E}} = 0 \ . \tag{13}$$

In the Appendix, Eq. (13) is developed when the solid volume fraction tends to ϕ. It returns a constraint for the electrostatic energy density, U_ε, involved in the ER mechanism, which can be written as

$$U_\varepsilon = -A_u \frac{\gamma}{\gamma + 1} (\hbar\omega_d)(\hbar\omega_l)(\hbar\omega_c)^2 \ , \tag{14}$$

γ being the Gruneisen parameter [20] and A_u a constant value. In the next section, we discuss and apply Eq. (14) to experimental data such as τ_0 versus ϕ coming from ER systems.

Results and discussion

Recently, the viscosity of a macroscopic medium was interpreted in terms of a collective quasi-particle population, which couples Brownian diffusion to quantum vibrational motions [3]. As expected, this mechanism would basically be characteristic of the liquid state of matter (Fig. 3), where Brownian and phonon wave diffusions are equally relevant. Here, on the basis of Eq. (14), applying an electric field to an ER medium results in the creation of bound energy states. Thus, we can sketch viscosity and yield stress increases in terms of vibrating strings (the fibrous columnar structures, Fig. 2) that are bound to the medium according to a threefold semiclassical coupling process. It involves the characteristic frequency (ω_c), phononlike ($\omega_d\omega_c$) and polariton-like ($\omega_l\omega_c$) waves, and increases its intensity with increasing γ (i.e., with $\frac{\gamma}{1+\gamma}$). The Gruneisen parameter gives, therefore, an indication of

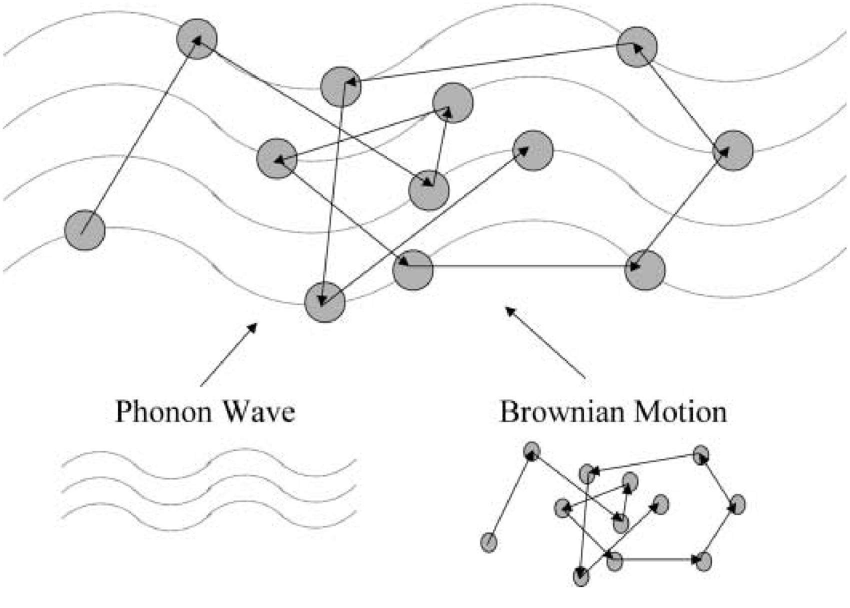

Fig. 2 Scheme of the quasi-particle mechanism proposed in momentum transport phenomena occurring in liquidlike systems [3]

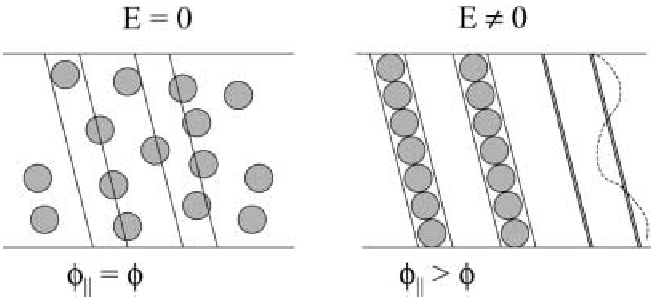

Fig. 3 Scheme of the electrically induced columnar structure as strings at the highest density value, vibrating in and bound to the ER medium

the efficiency with which the vibrational energy is exploited by the ER process or, equivalently, of the elastic rigidity loss (say, $\frac{1}{1+\gamma}$) associated with the particle chains. Consider now the dependence of the yield stress upon the solid volume fraction, $\tau_0 = \tau_0(\phi)$. For small deformations, the particle alignments confer to the fluid the character of an elastic solid (thus well described by Eqs. 1, 4) and are able to sustain a stress with no continuous deformations [22]. In fact, the steady-shear behaviour of an ER dispersion is normally well modeled as Bingham ($\beta = 1$, see later) or Casson ($\beta = \frac{1}{2}$) plastics [15, 23]:

$$\tau^{\beta}(\dot{\gamma}, \bar{E}, \phi) = [\eta(\phi)\dot{\gamma}]^{\beta} + \tau_0^{\beta}(\bar{E}, \phi) \ , \tag{15}$$

where τ, η and $\dot{\gamma}$ are the dynamic stress, the apparent viscosity and the rate of shear, respectively. To express ω_c, we note that the characteristic time must be proportional to some negative power law of the volume fraction [24] and, accordingly, we write

$$\omega_c = \bar{\omega}_c \phi^a \tag{16}$$

with $\bar{\omega}_c$ independent of ϕ and a being a positive heuristic coefficient. On the other hand, we can describe Debye ($j = \mathrm{d}$) and longitudinal ($j = \mathrm{l}$) optical phonon frequencies by an average combinations of contributions originating from the initial solid (s) and liquid (l) phases, namely [25]:

$$\frac{1}{\omega_j} = \frac{x}{\omega_{j\mathrm{s}}} + \frac{1-x}{\omega_{j\mathrm{l}}} \ , \tag{17}$$

with $x(\phi) = \frac{\phi}{\phi + \bar{r}(l-\phi)}$ being the atomic concentration of the suspended phase and $\bar{r} = \frac{v_s}{v_l}$ the molar volume ratio [3]. In the Appendix, we develop Eq. (14) exactly and then, to reduce the number of phenomenological coefficients, introduce an average law with two overall frequency values. Taking $\tau_0 \propto |U_\varepsilon|$ [15], we achieve in the end

$$\tau_0(\phi) = A_\tau \theta^2(\phi)\phi^{\alpha} \ , \tag{18}$$

where A_τ is a heuristic yield stress parameter, $\theta(\bar{r}, u_l, u_s; \phi) = \frac{\phi + \bar{r}(1-\phi)}{[u_l\phi + \bar{r}u_s(1-\phi)]}$ and $\alpha = 2a$. The nondimensional quantities $u_{l,s} \propto \hbar\bar{\omega}_{l,s}$ take into account the mean energies associated with $\bar{\omega}_{l,s}$. Unfortunately, the dielectric particles are usually imbedded in (nonconducting) oils [1], which do not possess a well-defined molecular weight. Moreover, the current literature does not report phonon spectra for ER fluids, where the theoretical evaluation of Debye, longitudinal and transverse phonon frequencies represents a tough task (in a simple liquid, for example, their analytical expressions involve pair correlation functions and the first two derivatives of the interparticle potential) [26]. This means that $\bar{r}$ and $u_{l,s}$ in Eq. (18) should be mainly regarded as phenomenological parameters. As expected, note that θ depends on the massive features of the medium ($\bar{r}$) and two cross-terms, coupling phonon and polariton waves on the basis of the geometrical distribution of solid and liquid phases. While ω_c is basically related to the probability to find a solid particle, θ gives an indication of the suspension state. If the relation between parameters is $u_s \geq u_l$, τ_0 always increases with ϕ, since $\frac{\partial\theta}{\partial\phi} \propto \bar{r}$ $(u_s - u_l) \geq 0$. When $u_l \geq u_s$, increasing the solid fraction decreases the strength of the bound states, and two antagonistic effects take place. In this case, as soon as ϕ exceeds a given critical fraction, θ can dominate ω_c and τ_0 decreases with increasing ϕ. This behaviour is more realistic and representative of what is frequently observed in ER suspensions and is explained in terms of the restoring force between particles in a chain. When the volume fraction is sufficiently large, chains get closer and start to interact electrostatically, decreasing the energy change required to break up a particle pair and so the solid character of the medium [22]. As an example, Eq. (18) was applied in Fig. 4 to account for some experimental investigations. They refer to hollow silica spheres in corn oil (Fig. 4a, b) [22], polyaniline particles in silicon oil (Fig. 4c) [27], emulsions consisting of chlorinated paraffin in silicon oil (Fig. 4d) [28] and numerical simulations (Fig. 4e) [29]. The number of best-fit coefficients, reported here in the captions to the figure, were reduced in cases a–c and e by fixing $A_\tau = 1$ Pa and constraining the parameters $\bar{r}$, α and the ratio between apparent energies to the same value. Particularly, in case d, τ^* measurements are normalized to the yield stress value just prior to the application of $\bar{E}$. We omitted points at $\phi \geq 0.8$, because they were affected by relevant uncertainties (26–41%). In case d, the data were obtained for several particle–fluid dielectric constant ratios, $\frac{\varepsilon_s}{\varepsilon_l}$, and nondimensionalized by $2\varepsilon_l(\tilde{\beta}E)^2$, where $\tilde{\beta} = \frac{\varepsilon_s - \varepsilon_l}{\varepsilon_s - 2\varepsilon_l}$ is the relative solid particle polarizability. In the end, it can be seen the agreement is quite satisfactory in all the cases examined here.

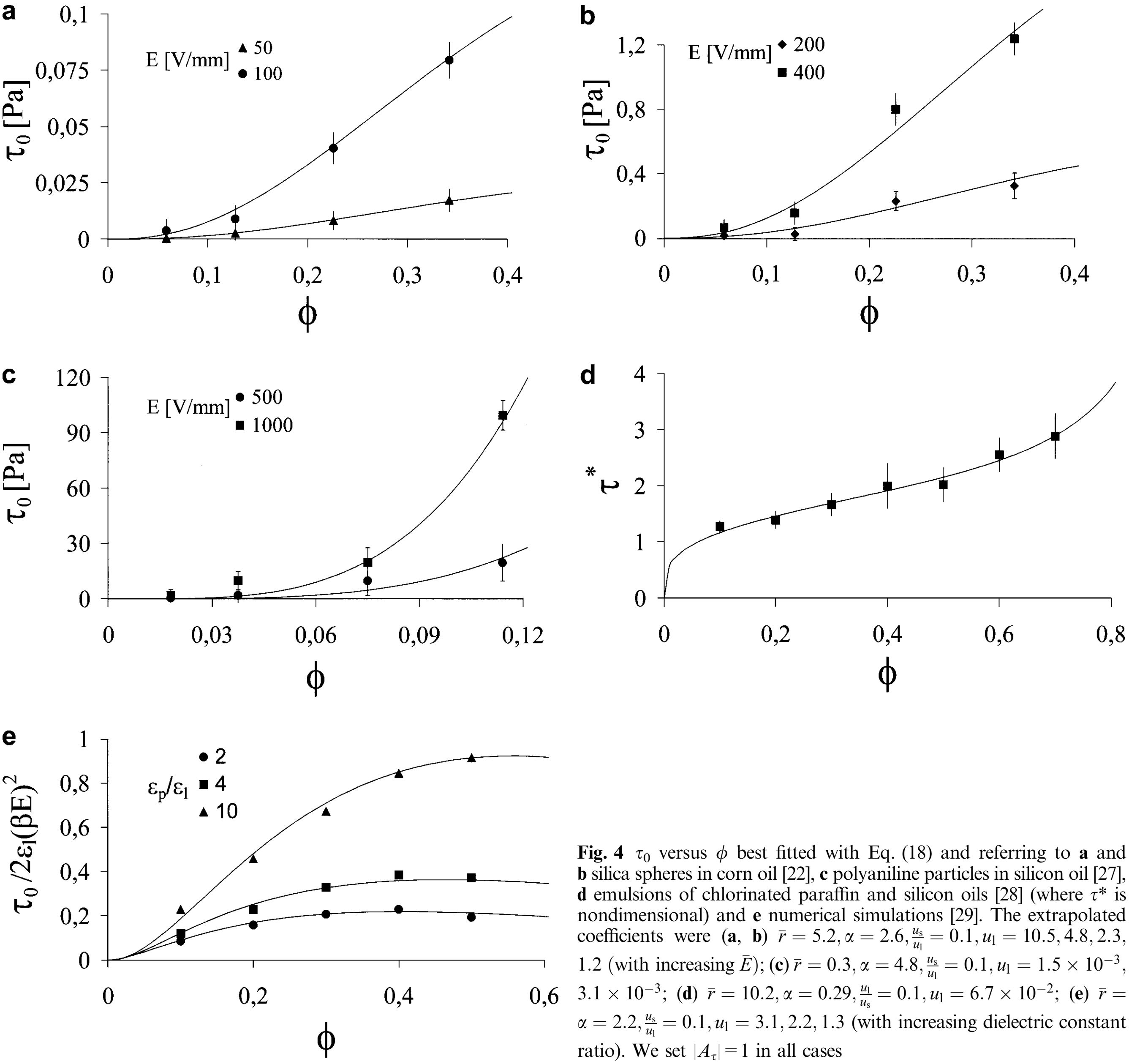

Fig. 4 τ_0 versus ϕ best fitted with Eq. (18) and referring to **a** and **b** silica spheres in corn oil [22], **c** polyaniline particles in silicon oil [27], **d** emulsions of chlorinated paraffin and silicon oils [28] (where τ^* is nondimensional) and **e** numerical simulations [29]. The extrapolated coefficients were (**a**, **b**) $\bar{r} = 5.2, \alpha = 2.6, \frac{u_s}{u_l} = 0.1, u_l = 10.5, 4.8, 2.3,$ 1.2 (with increasing $\bar{E}$); (**c**) $\bar{r} = 0.3, \alpha = 4.8, \frac{u_s}{u_l} = 0.1, u_l = 1.5 \times 10^{-3},$ 3.1×10^{-3}; (**d**) $\bar{r} = 10.2, \alpha = 0.29, \frac{u_l}{u_s} = 0.1, u_l = 6.7 \times 10^{-2}$; (**e**) $\bar{r} = \alpha = 2.2, \frac{u_s}{u_l} = 0.1, u_l = 3.1, 2.2, 1.3$ (with increasing dielectric constant ratio). We set $|A_\tau| = 1$ in all cases

Conclusions

1. A semiclassical approach was proposed to investigate the dramatic change in rheological properties observed in ER fluids upon application of an electric field. The Helmholtz free energy, written as the sum of phonon and dielectric contributions, was developed at some characteristic frequency scale of the ER medium and was used to get a stationary condition with respect to density variations induced by the field.
2. A bound energy density, involving a Gruneisen parameter, Debye, optical and characteristic medium frequencies, was obtained and related phenomenologically to the solid concentration (ϕ) dependence of the suspension yield stress (τ_0).
3. Rheological data τ_0 versus ϕ obtained from silica/corn oil, chlorinated paraffin/silicon oil and polyaniline/silicon oil systems and from numerical simulations were described.
4. It is suggested that the ER effect can be described in terms of a coupling between phononlike and

polariton-like waves that propagate across the solid–liquid medium.

5. Viscous phenomena were regarded as originating from a coupling between Brownian and collective quasi-particle motions.

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Appendix

In Eq. (9), one has to calculate $F_{\Omega\varepsilon} = \frac{\varepsilon_\infty v \bar{E}^2_{\tilde{\varepsilon}}}{2\pi\omega_\mathrm{l}} S$, where $S = S(\omega)$ is

$$S = \int \frac{\omega_\mathrm{l}^2 - \omega^2}{(\omega_\mathrm{t}^2 - \omega^2)[\tilde{\varepsilon}^2 + (\omega - \omega_\mathrm{c})^2]} \mathrm{d}\omega \ . \tag{A1}$$

Its primitive function consists of a sum of four contributions:

$$S = S_1 + S_2 + S_3 + S_4 \ , \tag{A2}$$

where if $o_\omega = \left(\tilde{\varepsilon}^2 + \omega_\mathrm{c}^2 + \omega_\mathrm{t}^2\right)^2 - 4\omega_\mathrm{c}^2\omega_\mathrm{t}^2$, we simply have

$$S_1 = \frac{\omega_\mathrm{l}^2 - \omega_\mathrm{t}^2}{\tilde{\varepsilon} o_\omega} \Bigg[(\tilde{\varepsilon}^2 - \omega_\mathrm{c}^2 + \omega_\mathrm{l}^2) \arctan\left(\frac{\omega - \omega_\mathrm{c}}{\tilde{\varepsilon}}\right) + \omega_\mathrm{c} \tilde{\varepsilon} \ln |\omega^2 + \tilde{\varepsilon}^2 + \omega_\mathrm{c}^2 - 2\omega_\mathrm{c}\omega| \Bigg] \ , \tag{A3}$$

$$S_2 = \frac{\omega_\mathrm{l}^2}{\tilde{\omega}_\mathrm{t}^2} \arctan\left(\frac{\omega - \omega_\mathrm{c}}{\tilde{\varepsilon}}\right) \ , \tag{A4}$$

$$S_3 = \frac{\omega_\mathrm{t}^2 - \omega_\mathrm{l}^2}{2\omega_\mathrm{t} o_\omega} (\omega_\mathrm{t}^2 + \tilde{\varepsilon}^2 + \omega_\mathrm{c}^2) \ln \left| \frac{\omega - \omega_t}{\omega + \omega_\mathrm{t}} \right| \ , \tag{A5}$$

$$S_4 = \frac{\omega_\mathrm{t}^2 - \omega_\mathrm{l}^2}{o_\omega} \omega_\mathrm{c} \ln \left| \omega^2 - \omega_\mathrm{t}^2 \right| \ . \tag{A6}$$

Considering $\tilde{\varepsilon} \ll \omega_\mathrm{c} \ll \omega_{\mathrm{d,l,t}}$ [3] and the integration domain (ω_c, ω_l) in Eq. (A1), enables us to approximate $S \simeq S_2$. For a nonionic crystal, $\omega_\mathrm{l} = \omega_\mathrm{t}$, so $S \equiv S_2$, identically. In this way, using Eq. (11) and the asymptotic condition $\frac{\omega_\mathrm{l}}{\tilde{\varepsilon}} \simeq \frac{\pi}{2}$, we have

$$F_{\Omega\varepsilon} \simeq \frac{v \varepsilon_0 \bar{E}^2 v}{4\omega_\mathrm{l}} \ , \tag{A7}$$

where we averaged over the macroscopic sample volume, v, and introduced the electric field applied externally, $E \simeq \bar{E}$.

To describe the condition

$$\left(\frac{\partial F_\Omega}{\partial \rho}\right)_{T,\bar{E}} = 0 \tag{A8}$$

we observe that, when the temperature is high enough, $|\ln(\beta\hbar\omega)| \gg 1$,

$$\left(\frac{\partial F_{\Omega 0}}{\partial \rho}\right)_{T,\bar{E}} = \alpha_{1\mathrm{u}} \frac{\omega_\mathrm{c}^2 \omega_\mathrm{d}}{\rho^2} \ln(\beta\hbar\omega_\mathrm{d}) \left[\gamma\left(3 + \frac{1}{\ln(\beta\hbar\omega_\mathrm{d})}\right) - 1\right] \simeq \alpha_{1\mathrm{u}} \frac{\gamma \omega_\mathrm{c}^2 \omega_\mathrm{d}}{\rho^2} \tag{A9}$$

and

$$-\left(\frac{\partial F_{\Omega\varepsilon}}{\partial \rho}\right)_{T,\bar{E}} = \alpha_{2\mathrm{u}} \frac{\varepsilon_0 \bar{E}^2}{\rho^2 \omega_\mathrm{l}} (\gamma + 1) \ , \tag{A10}$$

with $a_{1\mathrm{u}} = \frac{-m\tilde{\sigma}_{0v}}{\pi\tilde{\varepsilon}}$ and $a_{2\mathrm{u}} = \frac{mv}{4}$.

Note that $\tilde{\varepsilon}$ has been regarded as a constant, $\left|\frac{\delta_{\tilde{\varepsilon}}}{\tilde{\varepsilon}}\right| \ll \left|\frac{\delta\omega_\mathrm{c}}{\omega_\mathrm{c}}\right|$ [3], while γ denotes the overall Gruneisen parameter $\gamma = \frac{\partial \ln \omega_k}{\partial \ln \rho}$ for any normal mode k and in a system at fixed mass value [20]. Equation (14) follows from Eqs. (A9) and (A10) by calculating the electrostatic energy density from its definition, $U_\varepsilon \propto \varepsilon_0 \bar{E}^2$ and setting $A_\mathrm{u} \equiv \frac{a_{1\mathrm{u}}}{2a_{2\mathrm{u}}\hbar^4} = \frac{2\widetilde{\sigma_0 v}}{\pi\tilde{\varepsilon}v\hbar^4}$.

To calculate the bound energy in Eq. (14), consider Eq. (16),

$$\omega_\mathrm{c} = \bar{\omega}_\mathrm{c} \phi^a \ , \tag{A11}$$

and Eq. (17) ($j = \mathrm{l}$, s),

$$\frac{1}{\omega_j} = \frac{x}{\omega_{j\mathrm{s}}} + \frac{1 - x}{\omega_{j\mathrm{l}}} \ . \tag{A12}$$

After some algebraical elaborations, we get ($\alpha = 2a$)

$$|U_\varepsilon| = \frac{A_\mathrm{u}\gamma\phi^\alpha}{1 + \gamma} \frac{[r_\mathrm{s}\phi + r_\mathrm{l}(1 - \phi)]^2 \omega_\mathrm{dl}\omega_\mathrm{ds}\omega_\mathrm{ll}\omega_\mathrm{ss}\bar{\omega}_\mathrm{c}^2}{[\omega_\mathrm{dl} r_\mathrm{s}\phi + \omega_\mathrm{ds} r_\mathrm{l}(1 - \phi)][\omega_\mathrm{ll} r_\mathrm{s}\phi + \omega_\mathrm{ls} r_\mathrm{l}(1 - \phi)]} \ . \tag{A13}$$

Using $\bar{\omega}_{\mathrm{l,s}}$ two overall liquid and solid frequency contributions, enables us to transform Eq. (A13) into a simplified form:

$$|U_\varepsilon| = \frac{A_\mathrm{u}\gamma\phi^\alpha}{1 + \gamma} \left(\frac{r_\mathrm{s}\phi + r_\mathrm{l}(1 - \phi)}{\hbar\bar{\omega}_\mathrm{l} r_\mathrm{s}\phi + \hbar\bar{\omega}_\mathrm{s} r_\mathrm{l}(1 - \phi)}\right)^2 \times (\hbar\bar{\omega}_\mathrm{l})^2 (\hbar\bar{\omega}_\mathrm{s})^2 (\hbar\bar{\omega}_\mathrm{c})^2 \ , \tag{A14}$$

which gives us the phenomenological Eq. (14), upon setting $\tau_0 \approx\propto |U_\varepsilon|$, introducing the coefficient A_τ and defining $\bar{r} \equiv \frac{v_\mathrm{s}}{v_\mathrm{l}}$, $u_{\mathrm{l,s}} \propto \hbar\bar{\omega}_{\mathrm{l,s}}$ and $\theta = \frac{\phi + \bar{r}(1 - \phi)}{u_\mathrm{l}\phi + \bar{r}u_\mathrm{s}(1 - \phi)}$.

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