New nonlinear dielectric materials: Linear electrorheological fluids under the influence of electrostriction

J. P. Huang
Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong and Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany
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The usual approach to the development of new nonlinear dielectric materials focuses on the search for materials in which the components possess an inherently large nonlinear dielectric response. In contrast, based on thermodynamics, we have presented a first-principles approach to obtain the electrostriction-induced effective third-order nonlinear susceptibility for electrorheological (ER) fluids in which the components have inherent *linear*, rather than nonlinear, responses. In detail, this kind of nonlinear susceptibility is in general of about the same order of magnitude as the compressibility of the linear ER fluid at constant pressure. Moreover, our approach has been demonstrated to be in excellent agreement with a different statistical method. Thus, such *linear* ER fluids can serve as a new nonlinear dielectric material.

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Nonlinear materials with large values of the third-order nonlinear susceptibility χ [1] are in great need in industrial applications, such as nonlinear optical switching devices for use in photonics and real-time coherent optical signal processors, and new types of nonlinear dielectric materials are needed for use in electronic and microwave components and sensor windows. It is usually believed that an effective nonlinear dielectric response can appear in a composite material in which at least one component should possess an inherent *nonlinear* response. Thus, the common way to develop new nonlinear dielectric materials is to seek materials in which the components possess an inherently large nonlinear response [2]. In contrast, by using a first-principles approach based on thermodynamics, we shall present a quite different method to obtain a nonlinear dielectric response from electrorheological (ER) fluids in which the components possess inherent *linear* responses only (namely, linear ER fluids), under the influence of electrostriction. Thus, such linear ER fluids can also serve as a nonlinear dielectric material because an effective third-order nonlinear susceptibility can be induced due to the electrostriction effect. For clarity, it is worth noting that the above-mentioned linear ER fluids represent ER fluids whose dielectric constants are independent of the external electric field.

When an ER fluid [3–7] is subjected to a strong external field, elongated chains or columns of polarizable dielectric particles (e.g., titanium particles) form immediately parallel to the field due to the anisotropic long-range particle interaction inside the liquid carrier (e.g., silicone or corn oil). Because of this sort of rapid field-induced aggregation, recently ER fluids have received much attention [4–7] in both scientific research and industrial applications. For instance, ER fluids were also proposed as a method of constructing shock absorbers on magnetically levitated trains.

Let us start by considering what the electrostriction effect is for ER fluids. In the presence of an inhomogeneous electric field $\mathbf{E}$, it is known that a translational force $\mathbf{F}_t$ is exerted on a particle, given by

$$\mathbf{F}_t = \alpha \mathbf{E} \cdot \nabla \mathbf{E}, \tag{1}$$

where α represents the polarizability of the particle. Therefore, an inhomogeneous field acting on an ER fluid causes a particle concentration gradient with high concentrations at high field strengths. Next, if the ER fluid is situated partially in a strong external electric field at constant pressure, the density of the ER fluid in the field will increase accordingly due to the interaction between the induced dipole moment inside the particles and the electric field, which in turn yields an increase in the effective dielectric constant. This effect is called electrostriction. In fact, the phenomenon of electrostriction has been extensively studied, e.g., for dipolar fluids [8], near-critical sulfur hexafluoride in microgravity [9], ferroelectric liquid-crystalline elastomers [10], and an all-organic composite consisting of polyvinylidene fluoride trifluoroethylene copolymer matrix and copper-phthalocyanine particles [11]. Regarding the ER system, one [12] studied the electrostriction of solid ER composites in an attempt to apply them in sensing shear stresses and strains in active damping of vibrations due to the high sensitivity of ER composites to shear electrostriction. To the best of our knowledge, there is neither theoretical nor experimental research which treats the electrostriction effect of ER fluids. In this paper, based on thermodynamics we shall present a first-principles approach to derive the electrostriction-induced effective nonlinear third-order susceptibility χ of linear ER fluids.

For investigating the electrostriction effect, take the experimental situation as follows. There is a capacitor with volume V_c, in which the electric field and the dielectric displacement are denoted by E_c and D_c, respectively. Both of them should satisfy the usual electrostatic equations, namely,

$$\nabla \cdot \mathbf{D}_c = 0, \tag{2}$$

$$\nabla \times \mathbf{E}_c = 0. \tag{3}$$

Here Eq. (3) implies that the electric field $\mathbf{E}_c$ can be expressed as the gradient of a potential ϕ,

$$\mathbf{E}_c = -\nabla\phi. \tag{4}$$

Under the appropriate boundary condition, the inhomogeneous ER fluid (in the capacitor) can be represented as a region of volume V_c, surrounded by a surface S_s. This kind of boundary condition is

$$\phi = -\mathbf{E}\cdot\mathbf{R} \quad \text{on } S_s, \tag{5}$$

which, if the ER fluid within V_c were uniform, would give rise to an electric field which is identical to $\mathbf{E}$ everywhere within V_c. As a matter of fact, even in an inhomogeneous ER fluid with this boundary condition, the volume average of the electric field $\langle\mathbf{E}_c\rangle$ within V_c still equals that of the external field $\langle\mathbf{E}\rangle$, i.e.,

$$\langle\mathbf{E}_c\rangle = \frac{1}{V_c}\int \mathbf{E}_c(\mathbf{R})\mathrm{d}^3r = \langle\mathbf{E}\rangle. \tag{6}$$

It is worth noting that in this case there is no applied field outside the capacitor. Also, the whole ER fluid with volume V is situated both inside and outside the capacitor at a constant pressure p.

In the presence of the inhomogeneous external electric field $\mathbf{E}$, the effective linear dielectric constant ϵ_e and effective third-order nonlinear susceptibility χ for the ER fluid inside the capacitor are defined as

$$\langle\mathbf{D}_c\rangle = \epsilon_e\langle\mathbf{E}\rangle + 4\pi\chi|\langle\mathbf{E}\rangle|^2\langle\mathbf{E}\rangle, \tag{7}$$

where $\langle\cdots\rangle$ denotes the volume average of $\cdots$. A similar definition [13] was used for a composite material which is subjected to a homogeneous external electric field. In view of the real quantities under consideration, Eq. (7) can be rewritten as

$$\langle\mathbf{D}_c\rangle = \epsilon_e\langle\mathbf{E}\rangle + 4\pi\chi\langle\mathbf{E}\rangle^2\langle\mathbf{E}\rangle. \tag{8}$$

On the other hand, based on thermodynamics the effective dielectric constant ϵ_E including the incremental part due to the electrostriction is defined as

$$\epsilon_E \equiv \left(\frac{\partial\langle\mathbf{D}_c\rangle}{\partial\langle\mathbf{E}\rangle}\right)_{T,p} = \left(\frac{\partial\langle\mathbf{D}_c\rangle}{\partial\langle\mathbf{E}\rangle}\right)_{T,\rho} + \int f(d)\left(\frac{\partial\langle\mathbf{D}_c\rangle}{\partial\rho(d)}\right)_{T,\langle\mathbf{E}\rangle} \times\left(\frac{\partial\rho(d)}{\partial\langle\mathbf{E}\rangle}\right)_{T,p}\mathrm{d}d, \tag{9}$$

where $\rho(d)$ stands for the density of the particles with diameter d, and T is the temperature. Here $(\partial\langle\mathbf{D}_c\rangle/\partial\langle\mathbf{E}\rangle)_{T,\rho}$ corresponds to the effective linear dielectric constant, namely, ϵ_e. In Eq. (9), $f(d)$ denotes a specific size distribution which exists in real ER fluids [14], e.g., the lognormal distribution $f(d) = (1/\sqrt{2\pi}\sigma d)\exp\{-[\ln^2(d/\delta)]/2\sigma^2\}$, where σ is the standard deviation and δ the median diameter.

Accordingly, the incremental dielectric constant due to the electrostriction [the last term of Eq. (9)] is equivalent to $12\pi\chi\langle\mathbf{E}\rangle^2$. That is,

$$12\pi\chi\langle\mathbf{E}\rangle^2 = \int f(d)\left(\frac{\partial\langle\mathbf{D}_c\rangle}{\partial\rho(d)}\right)_{T,\langle\mathbf{E}\rangle}\left(\frac{\partial\rho(d)}{\partial\langle\mathbf{E}\rangle}\right)_{T,p}\mathrm{d}d. \tag{10}$$

Let us take one step forward to rewrite Eq. (10) as

$$\chi\langle\mathbf{E}\rangle^2 = \frac{1}{12\pi}\int f(d)\langle\mathbf{E}\rangle\left(\frac{\partial\epsilon_e}{\partial\rho(d)}\right)_{T,\langle\mathbf{E}\rangle}\left(\frac{\partial\rho(d)}{\partial\langle\mathbf{E}\rangle}\right)_{T,p}\mathrm{d}d. \tag{11}$$

The differential increase of the density inside the capacitor $\mathrm{d}\rho(d)$ corresponds to the increase in mass equal to $V_c\mathrm{d}\rho(d)$. Naturally, this increase in mass is equal to a decrease in mass outside the capacitor, which is given by $-\rho(d)\mathrm{d}(V-V_c) = -\rho(d)\mathrm{d}V$, so that $\mathrm{d}\rho(d) = -[\rho(d)/V_c]\mathrm{d}V$. Consequently, we may rewrite Eq. (11) as

$$\chi\langle\mathbf{E}\rangle^2 = -\frac{1}{12\pi}\int f(d)\langle\mathbf{E}\rangle\frac{\rho(d)}{V_c}\left(\frac{\partial\epsilon_e}{\partial\rho(d)}\right)_{T,\langle\mathbf{E}\rangle}\left(\frac{\partial V}{\partial\langle\mathbf{E}\rangle}\right)_{T,p}\mathrm{d}d. \tag{12}$$

Next, we can obtain $(\partial V/\partial\langle\mathbf{E}\rangle)_{T,p}$ by using the differential of the free energy $\mathrm{d}F$,

$$\mathrm{d}F = -p\,\mathrm{d}V - S\,\mathrm{d}T + \frac{V_c}{4\pi}\langle\mathbf{E}\rangle\mathrm{d}\langle\mathbf{D}_c\rangle, \tag{13}$$

where S denotes the entropy. In view of the transformed free enthalpy G

$$G = F + pV - \frac{V_c}{4\pi}\langle\mathbf{E}\rangle\langle\mathbf{D}_c\rangle, \tag{14}$$

the differential of G admits the form

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p - \frac{V_c}{4\pi}\langle\mathbf{D}_c\rangle\mathrm{d}\langle\mathbf{E}\rangle. \tag{15}$$

Based on this equation, we obtain

$$\left(\frac{\partial V}{\partial\langle\mathbf{E}\rangle}\right)_{T,p} = -\frac{V_c\langle\mathbf{E}\rangle}{4\pi}\left(\frac{\partial\epsilon_e}{\partial p}\right)_{T,\langle\mathbf{E}\rangle}. \tag{16}$$

Then, the substitution of Eq. (16) into Eq. (12) yields

$$\chi\langle\mathbf{E}\rangle^2 = \frac{1}{48\pi^2}\int f(d)\langle\mathbf{E}\rangle^2\rho(d)\left(\frac{\partial\epsilon_e}{\partial\rho(d)}\right)_{T,\langle\mathbf{E}\rangle}\left(\frac{\partial\epsilon_e}{\partial p}\right)_{T,\langle\mathbf{E}\rangle}\mathrm{d}d. \tag{17}$$

Now let us use

$$\left(\frac{\partial\epsilon_e}{\partial p}\right)_{T,\langle\mathbf{E}\rangle} = \beta\rho(d)\left(\frac{\partial\epsilon_e}{\partial\rho(d)}\right)_T, \tag{18}$$

where

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{19}$$

denotes the compressibility in the absence of the external electric field. For deriving Eq. (18), we have neglected the terms which depend on $\langle\mathbf{E}\rangle$ because they lead to terms in powers of $\langle\mathbf{E}\rangle$ higher than the second in Eq. (17). In the light of the same approximation, the substitution of Eq. (18) into Eq. (17) leads to

$$\chi\langle\mathbf{E}\rangle^2 = \frac{1}{48\pi^2}\int f(d)\langle\mathbf{E}\rangle^2\beta\rho(d)^2\left(\frac{\partial\epsilon_e}{\partial\rho(d)}\right)_T^2 \mathrm{d}d. \quad (20)$$

So far, the effective third-order nonlinear susceptibility χ of the ER fluid is given by

$$\chi = \frac{\beta}{48\pi^2}\int f(d)\rho(d)^2\left(\frac{\partial\epsilon_e}{\partial\rho(d)}\right)_T^2 \mathrm{d}d. \quad (21)$$

For determining the effective linear dielectric constant ϵ_e, we can resort to the anisotropic Maxwell-Garnett theory, namely,

$$\frac{g_L(\epsilon_e-\epsilon_2)}{\epsilon_2+g_L(\epsilon_e-\epsilon_2)} = \frac{4\pi}{3}\int f(d)\frac{\rho(d)}{m(d)}\alpha(d)\mathrm{d}d, \quad (22)$$

where $m(d)$ $[\alpha(d)]$ denotes the mass (polarizability) of the individual particle with diameter d, and ϵ_2 the dielectric constant of the carrier liquid. It is known that in the presence of an electric field, a particle chain can be formed in the direction of the field, and thus structural anisotropy should appear inside this ER fluid. Accordingly, in Eq. (22) g_L ($g_L \geqslant 1/3$) is the local field factor in the longitudinal field case, which was measured by using computer simulations [15], satisfying the sum rule $g_L+2g_T=1$ [16]. Here g_T represents the local field factor in the transverse field case. As $g_L=1/3$, the usual Clausius-Mossotti equation is recovered, which is valid for an isotropic system. In fact, the degree of anisotropy of the present system is measured by how far g_L deviates from $1/3$.

Equation (21) is the main result of the present paper. In detail, the electrostriction-induced third-order nonlinear susceptibility χ can be expressed in terms of the size distribution function and density of the particles, the effective linear dielectric constant, etc. In particular, it is apparent that at constant pressure χ is proportional to the compressibility of the ER fluids of interest. More precisely, χ is of about the same order of magnitude as the compressibility, which can be readily measured in experiments. Let us compute χ for a real example of an ER fluid given by Klingenberg *et al.* [17]. In detail, this monodisperse ER fluid contains hollow silica spherical particles embedded in corn oil. The parameters obtained from the experiment are diameter of the particles 95 μm, $\epsilon_2=2.9$, dielectric constant of the particles 11, volume fraction of the particles 0.26, apparent density 0.74 g/mL, and density of the corn oil 0.92 g/mL. Based on these parameters, it is straightforward to obtain $\alpha=1.5\times10^{-7}$ cm^3, $\rho=0.228$ g/cm^3, and $m=1.02\times10^{-7}$ g. If we take $g_L=1/8$, $\chi=83.7\beta$. Further, as $\beta=2.1\times10^{-10}$ Pa^{-1}, $\chi=1.76\times10^{-9}$ (V/cm)$^{-2}$. Interestingly, Eq. (21) has exactly bridged the mechanical properties and nonlinear dielectric properties of linear ER fluids. In other words, the mechanical properties give rise to nonlinear dielectric responses (third-order nonlinear susceptibilities) of linear ER fluids.

In what follows, we would like to show the correctness of the present theory by comparing with a different statistical method. First, let us derive the increase of the density $\Delta\rho$ due to electrostriction, based on $(\partial V/\partial\langle\mathbf{E}\rangle)_{T,p}$. Let us start from

$$\Delta\rho = \int\int_0^{\langle\mathbf{E}\rangle} f(d)\left(\frac{\partial\rho(d)}{\partial\langle\mathbf{E}\rangle}\right)_{T,p}\mathrm{d}\langle\mathbf{E}\rangle\mathrm{d}d. \quad (23)$$

To this end, we obtain

$$\Delta\rho = \frac{1}{8\pi}\int f(d)\langle\mathbf{E}\rangle^2\beta\rho(d)^2\left(\frac{\partial\epsilon_e}{\partial\rho(d)}\right)_T \mathrm{d}d. \quad (24)$$

Again, in the expression for $\Delta\rho$ terms in powers of $\langle\mathbf{E}\rangle$ higher than the second have been neglected. For the monodisperse case, Eq. (24) reduces to

$$\Delta\rho = \frac{1}{8\pi}\langle\mathbf{E}\rangle^2\beta\rho^2\left(\frac{\partial\epsilon_e}{\partial\rho}\right)_T. \quad (25)$$

Let us assume there is an ideal gas inside the capacitor. In this case, the compressibility is given by

$$\beta = \frac{M}{\rho RT}, \quad (26)$$

where M is the molecular weight, and R the molar gas constant. For the ideal gas (monodisperse case), setting $g_L=1/3$ in the above Clausius-Mossotti equation [Eq. (22)] yields

$$\frac{\epsilon_e-1}{\epsilon_e+2} = \frac{4\pi}{3}\frac{\rho}{m}\alpha. \quad (27)$$

In view of $\epsilon_e-1\ll1$ for ideal gases, we obtain

$$\left(\frac{\partial\epsilon_e}{\partial\rho}\right)_T = \frac{4\pi}{m}\alpha, \quad (28)$$

and hence the desired result for $\Delta\rho$,

$$\Delta\rho = \frac{\langle\mathbf{E}\rangle^2\rho\alpha}{2k_BT}. \quad (29)$$

This equation can also be achieved by using a statistical method. According to Boltzmann's distribution law, the number of moles per cm^3 of the gas at a point with field strength $\langle\mathbf{E}\rangle$ is given by

$$N = N'\exp\left(-\frac{W}{k_BT}\right), \quad (30)$$

where W denotes the average value of the work required to bring a molecule into the field $\langle\mathbf{E}\rangle$, and N' the number of moles per cm^3 of the gas at a point in the absence of field. It is straightforward to obtain

$$\Delta\rho = M(N-N') = \frac{\langle\mathbf{E}\rangle^2\rho\alpha}{2k_BT}, \quad (31)$$

which is exactly the same as Eq. (29). Again, the terms in higher powers of $\langle\mathbf{E}\rangle$ than the second have been neglected.

To sum up, by using thermodynamics we have presented a first-principles approach to the derivation of the effective third-order nonlinear susceptibility [Eq. (21)] of linear ER fluids under the influence of electrostriction, which is of about the same order of magnitude as the compressibility of the ER fluid at constant pressure. Our approach has been

demonstrated to be in excellent agreement with an alternative statistical method.

The aim of the present paper is to exploit electrostriction in a linear ER fluid in order to generate a nonlinear dielectric response. The proposed mechanism works for dc electric fields. It should also be expected to work for ac fields with frequency ν if the size of the sample is not greater than c_s/ν, where c_s is the sound velocity. In this connection, ν can be up to a kilohertz or so. Otherwise the required mass density oscillations will not be able to keep up with the rapid changes in the electric field.

The theory described in this paper can be used to study any colloidal suspension like magnetorheological fluids [18], ferrofluids [19], etc. Since there exist permanent magnetic dipole moments inside magnetorheological fluids and ferrofluids, the derivation of the effective linear permeability can still be done by using the present anisotropic Clausius-Mossotti equation, in which, however, terms for permanent magnetic moments should be added accordingly. In a word, we have shown theoretically that linear ER fluids under the influence of the electrostriction effect can serve as a new nonlinear dielectric material.

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