Abstract

Some 30 years ago the idea was born to mix nano-sized magnetic particles with nematic liquid crystals, in order to get fluids with a large magnetic susceptibility. Quite recently stable and well defined systems have been produced and it became evident that these emulsions are interesting materials not only because of their enhanced magnetic susceptibility. This thesis studies systematically the new, mainly dynamic, features of such ferronematics. It makes a number of theoretical predictions for qualitatively new effects that can be tested experimentally. The method used is that of phenomenological hydrodynamics and its extension to slowly relaxing, non-hydrodynamic variables. This is a well established method to get a reliable set of (partial differential) equations that describe the long wavelength and low frequency behavior of complex fluids and soft matter. It is phenomenological in the sense that parameters (susceptibilities and transport coefficients) are introduced, whose magnitude is not known a priori. Emphasis is laid, thus, on qualitatively new effects.

First, the possible phase structure of these materials has been investigated. Conventional ferrofluids do not show any phase transition and are "super"-paramagnetic at any temperature, particle concentration, or density and no transition. That means, there is a large (saturation) magnetization even for moderate or low external field strengths. No ferromagnetic state with a spontaneous magnetization has been observed. Ordinary nematic liquid crystals show a transition from an isotropic state to the nematic state (with orientational order) at a certain temperature (thermotropic) or concentration (lyotropic) in the case of solutions. The question was, what kind of phase transitions are possible in ferronematics with respect to both, nematic (orientational) and magnetic (ferromagnetic) order. Within a simple Landau free energy description up to fourth order in the appropriate order parameters it could be shown that there are two different ferronematic phases (apart from an isotropic one at high temperature or low concentration): one with nematic but no magnetic order (superparamagnetic) and one with both types of order. Within this model a phase with magnetic but no nematic order seems to be impossible. The transition from the isotropic to the ferromagnetic phase can be either directly or in two steps via the (super)paramagnetic nematic phase. Those transitions, where the nematic order is built, are always first order. In the presence of an external magnetic field the transitions are smeared out and at high fields can become second order. In an external magnetic field the behavior of a superparamagnetic and ferromagnetic phase are rather similar. Up to now no clear experimental evidence for a ferromagnetic phase has been found, but experiments at low or vanishing fields are rather scarce.

In a second step the macroscopic dynamics of (superparamagnetic) ferronematics has been explored. Generally, one has to consider the dynamics of the nematic degree of freedom (reorientation of the preferred direction in space) as well as the magnetic one (rotations and size changes of the magnetization). Since the latter usually is much faster than the former, one can consider the special case that the magnetization has already relaxed to its equilibrium value and direction (set by the external field). Then a ferronematic dynamics has the same structure as that of a conventional nematic liquid crystal. Only the static and dynamic response to external fields is much stronger. In conventional nematics the influence of a magnetic field on the dynamics had been neglected or not considered at all, previously. Here such dynamic effects

are studied systematically. They can be linear in the external field, in contrast to the static (superparamagnetic) effect, which has to be quadratic in the field due to time reversal invariance (of the free energy). In the dynamics, currents can be odd or even under time reversal, so describing reversible or irreversible behavior. Thus, the new linear dynamic field effects always toggle between reversible and irreversible, when compared to their non-magnetic counter parts. Among the effects discussed are reversible ("Hall'-like) contributions to heat, concentration, and thermodiffusion currents as well as viscosity and director relaxation, and an irreversible contribution to flow alignment effect. The latter is manifest in a shear flow experiment, with the magnetic field in the shear plane, where in a ferronematic the nematic director orients with a non-vanishing component out of the shear plane, while in conventional nematics the director orients in the shear plane. Another testable effect of a new linear dynamic effect is the relaxation of the director into a direction set by an external magnetic field. For conventional nematics this is a simple relaxation process, where the director and the magnetic field lie always in the same plane. In ferronematics an oscillation is superimposed on the relaxation connected with a spatial wobble.

In the more general case the dynamics of the magnetization has to be taken into account. Since the director can be either parallel or perpendicular to the field (and the magnetization) in equilibrium, there is a uniaxial and a biaxial case. The third possible case that the director, the magnetization and the magnetic field are all pointing in different directions, but lie in the same plane, is disregarded here, since it has not been found in experiment yet. The dynamics is rather rich: In addition to the coupling of the orientational changes of the magnetization and the nematic director reorientations, there are reversible and dissipative dynamic cross-couplings of compressional, shear and elongational flow with rotations and changes of the absolute value of the magnetization and director reorientations. For measuring some combinations of the parameters that describe these cross-couplings we studied the sound wave spectrum and the rheology of shear flow. In particular the sound spectrum is studied and a field-dependent contribution to damping is found. Additionally sound waves (compressional flow) can trigger shear flow (and vice versa), if the wave vector is oblique to the field direction. Oscillatory shear (without field, or with a field parallel or perpendicular to the wave vector) shows a considerable influence of the magnetic degree of freedom. Even without a magnetic field the apparent viscosity is different from the bare one and the modified nematic director diffusion couples to the flow response. In the presence of an external field the director relaxation is shifted to a finite frequency, which approximately increases with the third power of the field strength.

Finally the dynamics of ferrogels is investigated. Here the magnetic particles are put into a matrix of cross-linked polymers. Ferrogels can be isotropic or uniaxial depending whether the cross-linking process is done with or without a magnetic field, although we only deal with the former one. An external field leads to a static deformation of the gel (magnetostriction). The dynamic around this strained equilibrium state shows various peculiar features. The dynamic coupling of the magnetic degree of freedom to the elastic one leads to magnetic field dependent effective (longitudinal and transverse) sound velocities. The dispersion relations show characteristic steps at the frequency of the magnetization relaxation. This frequency and field dependence of the sound spectra, thus provides the opportunity to measure the relevant static and dynamic magneto-elastic parameters that are crucial for the possible applications of ferrogels.