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A mesoscopic rheological model of moderately concentrated colloids

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ABSTRACT

We extend the Maffettone–Minale model by including non-elliptical shapes of dispersed particles, a new family of internal forces controlling particle deformations, and particle–particle interactions. The last extension is made by transposing the way the chain-chain interactions are mathematically expressed in the reptation theory to suspensions. The particle–particle interactions are regarded as a confinement to cages formed by surrounding particles and by introducing a new dissipative motion (an analog of the reptation motion) inside the cages. Nonlinear responses to imposed shear and elongational flows are found to be in qualitative agreement with available experimental data.

1. Introduction

In this paper we are addressing rheology of colloidal dispersions (see e.g. [1,2] for a recent review). Our objective is twofold. First, we investigate relation between mesoscopic physics of dispersions and their rheological behavior. Our second objective is to illustrate the systematic formulation of governing equations of rheological models that is based on the requirement of compatibility of their solutions with mechanics (in the sense that the time reversible part of the time evolution is Hamiltonian) and with thermodynamics (in the sense that the entropy does not decrease during the time evolution).

The level of description on which we formulate the mesoscopic physics of dispersions in this paper is the level on which one symmetric three-by-three tensor (or possibly several of such tensors) serves as a state variable describing the internal structure. We call it *Hand level of description* since this type of the internal state variable appeared first in [3]. We shall use the symbol $\boldsymbol{c}$ to denote the tensor. After choosing $\boldsymbol{c}$ as the internal state variable, we have to decide what is its physical interpretation. Among many possibilities (see e.g. [4–9]), we choose in this paper to follow Maffettone and Minale in [10], and regard it as a mathematical representation of the ellipsoidal shape of the suspended particle. We call any rheological model on the Hand level of description with this physical interpretation of $\boldsymbol{c}$ as the Maffettone–Minale model (or in an abbreviated form MM-model).

What physics can we express in the MM-models? We begin with the most important physical feature. If we restrict ourselves to dispersed particles that are made of deformable but incompressible materials then the volume of the particle characterized by $\boldsymbol{c}$ has to remain constant during the time evolution. If we consider $\det \boldsymbol{c}$ as a measure of the volume of the ellipsoid associated with $\boldsymbol{c}$ then the constraint $\det \boldsymbol{c} = const.$ is the first, most important, physical feature of the MM-models. Next, we have to address the question of what are the forces that control the particle deformations. In this paper we take them to be the forces generated by the surface area of the particle. We show that this type of MM-models predicts rheological behavior that is in a good qualitative agreement with the experimental data reported in [11]. We then continue and introduce more complex physics into dispersions. In particular, we introduce: (i) more complex non-ellipsoidal shapes of the particles, (ii) particle–particle interactions, and (iii) new internal forces driving non-ellipsoidal deformations. The MM-model with these new features is called an extended MM-model or in an abbreviated form EMM-model.

Regarding the mathematical formulation of the model, particularly new is the way in which we are expressing the particle–particle interactions. This type of interactions, that together with large particle deformations may lead to a formation of an interconnected network of particles [12], is expected to play an important role in more dense dispersions. We are inspired by the reptation theory developed by de Gennes and Edwards [13,14] in which chain-chain interactions are seen as confinements to tubes (formed by surrounding chains) inside which a new dissipative motion, called reptation, takes place. In dispersions we replace tubes by cages

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(as it has been suggested on more microscopic levels of description in [15,16]) inside which a new dissipative motion (analogical to reptation) takes place.

We conclude the introduction by a comment about different levels of description. The Hand level that we are choosing in this paper is very much on the macroscopic end of the hierarchy of levels. On the other hand, the level of description chosen for example in [16]) in direct molecular simulations is on the opposite (microscopic) end. The advantage of more macroscopic theories is a large domain of applicability and a relative simplicity of the passage from governing equations to predictions that can directly be compared with experimental results. Their disadvantage is then an inevitable presence of material parameters which, due to a large "distance" from microscopic physics, are not directly related to microscopic characterizations of the particles. Given a specific colloid, their values representing it have to be found by considering some of the macroscopic observations as their measurements. The advantage of microscopic levels is the possibility to begin the analysis with a very clear and specific microscopic physics. The disadvantage is then small domain of validity (caused by the specificity of the microscopic physics entering the modeling) and the complexity of the passage to macroscopic levels on which the experimental observations are made. Such passage is inevitably involves largely ad hoc approximations needed for example to express macroscopic forces (as e.g. temperature gradient) in microscopic terms or to extract from the output of direct simulations (particle trajectories) the macroscopic information of direct interest. The modeling that has most advantages and the least disadvantages is a multilevel modeling pursued on several different levels of description.

2. Maffettone–Minale model

In this section we present the MM-model as a particular realization of GENERIC. The advantages of such presentation are the following: (i) the model, even before the modifications made in the subsequent section, is more general and more complete than the model introduced originally in [10], (ii) the intrinsic compatibility of the morphology time evolution with the expression for the stress tensor is guaranteed, and (iii) the extension of the MM-model needed to express more complex physics becomes straightforward (see Section 3).

First, we recall some basic elements of GENERIC. The objective of GENERIC is to make the reduction process leading from a microscopic insight to a mesoscopic model more systematic and transparent. The main idea is that before starting the reduction we make an assumption that the target mesoscopic equation possesses a certain structure. The requirement that the structure emerges in the reduction makes the reduction well organized. What is the structure of the mesoscopic time evolution equations and why it is required? We require it because it guarantees that solutions to equations possessing it agree with certain basic experimental observations like for instance conservations of mass, momentum and energy and observations constituting the experimental basis of thermodynamics. The mathematical formulation of the structure has emerged gradually. The mechanical content has been formulated in the abstract Hamiltonian structure (first for fluid mechanics equations [17] and for kinetic equations [18]) and the thermodynamic content in the structure of gradient dynamics (in [19–21]). Both structures have been then combined in [22–26]. A particular formulation of the combination (see (1) below) has been called GENERIC (an acronym for General Equation for Non-Equilibrium Reversible-Irreversible Coupling) in [27,28]. Geometrical and physical content of the structure has recently been discussed in [29].

In this paper we limit ourselves to suspensions that are kept at constant temperature. We recall therefore GENERIC only in this particular case. Let x stand for the set of state variables. The equation governing its time evolution has the general form

$$\frac{\partial x}{\partial t} = L(x)\Phi_x - \left[\frac{\partial \Xi}{\partial x^*}\right]_{x^*=\Phi_x} \tag{1}$$

The symbol $\Phi(x)$ stands for the free energy. The first term on the right hand side of (1) represents the Hamiltonian time evolution. The operator $L(x)$, called a Poisson bivector, expresses mathematically the kinematics of x. The properties that L is required to satisfy are best expressed by constructing with it a bracket $\{A,B\} = \langle A_x, L(x)B_x \rangle$ and requiring that it is a Poisson bracket (i.e. $\{A,B\} = -\{B,A\}$ and the Jacobi identity holds). The notation that we use in (1) and throughout the paper is the following: A and B are real valued sufficiently general functions of x, A_x denotes a derivative of A with respect to x, and $\langle , \rangle$ denotes scalar product. The Hamiltonian time evolution is thus an evolution generated by a potential (in the case of isothermal systems it is the free energy) in which the gradient of the potential (a covector field) is transformed into a vector field by the Poisson bivector L.

The second term on the right hand side represents the thermodynamic part of the time evolution. This time evolution is also generated by the free energy but the geometrical structure transforming its gradient into the vector field is different from the one playing this role in the Hamiltonian dynamics. We refer the reader who is interested in a more detailed physical and geometrical discussion of (1) to [29]. Here we only explain the notation: $\Xi(x,x^*)$ is the dissipation potential (see [21]), i.e. a potential satisfying: (i) $\Xi(x,0) = 0$ for all x; (ii) $\Xi(x,x^*)$ reaches its minimum as a function of x^* for all x; and (iii) $\Xi(x,x^*)$ is a convex function of x^* in a neighborhood of $x^* = 0$ for all x. We note that these properties guarantee that $\langle x^*, \Xi_{x^*} \rangle > 0$ which, together with the property $\langle \Phi_x, L(x)\Phi_x \rangle = 0$, implies that $\frac{d\Phi}{dt} > 0$ during the time evolution governed by (1).

We recognize in (1) four modules: **Module 1** *state variables* x, **Module 2** *their kinematics* L, **Module 3** *dissipation potential* Ξ, and **Module 4** *free energy* Φ.

In the rest of this paper we formulate a mesoscopic rheological model of soft colloids. We shall do it by expressing our physical insight into this type of fluids in the four modules listed above. The essential difference between this and the more usual derivation is that in the latter the physical insight is expressed directly in one step in the governing equation while in our derivation the process is gradual, module by module. The way the modules are then combined, according to (1), guarantees agreement of solutions of the governing equations with certain results of experimental observations.

2.1. Module 1: State variables x

The point of departure of any type of rheological modeling is always the choice of the level of description, or in other words, the choice of state variables. We have to decide how shall we express our physical insight mathematically. We can choose between microscopic levels on which we can directly follow details and more macroscopic levels on which only some selected aspects of the morphology are followed. Optimally, we want to follow only those details that are essential for our interest determined by our experimental observations and intended applications. Since we cannot know in advance of what type of physics is important and what can be ignored, the choice of state variables is always a trial-and-error procedure.

In this paper we decide to remain on a rather macroscopic level of description. The advantage of this choice is a wide range of