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The elasto-hydrodynamic equations of the colloidal crystals

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Résumé. — Nous donnons une dérivation théorique des équations du mouvement des cristaux colloïdaux. Suspension aqueuse ordonnée de particules colloïdales, un cristal colloïdal nécessite une description faisant appel à la fois à l'hydrodynamique et à l'élasticité. Partant des équations sans dissipation obtenues par Dzyaloshinskii et Volovick [1], nous y incluons les phénomènes dissipatifs en utilisant la théorie des phénomènes irréversibles. Nous obtenons des équations du mouvement analogues à celles des smectiques et qui, pour des situations proches de l'équilibre, redonnent les équations déjà utilisées dans la littérature. Ceci nous permet de montrer que les termes de perméation donnent lieu à une dissipation très importante.

Abstract. — We give a theoretical derivation of the equations of motion for colloidal crystals. Colloidal crystals are an aqueous suspension of colloidal particles which organize themselves in long-range-ordered crystals so that their description requires both hydrodynamic and elastic theory. We follow the approach given by Dzyaloshinskii and Volovick [1] for classical crystals and include the dissipation with the use of the theory of irreversible phenomena. We obtain a set of equations of motion which are analogous to the corresponding ones for the smectics. In the linear regime, these equations tend to the equations already in use for the description of colloidal crystals. We point out the importance of the permeation terms.

1. Introduction.

Colloidal crystals (CC) are aqueous suspensions of monodisperse colloidal particles which organize themselves with long-range-order. The particles used for most experiments are spherical aggregates of polymer chains with diameter \(d\) in the range \(d \sim 0.1-1 \mu m\) (for a survey see Ref. [2]). In water, dissociation reactions occur at the surface of the particles and provide a large negative electrostatic charge per particle of the order of \(Ze = 10^3 e\). All these particles interact with each other through a screened Coulomb interaction and as a result build a three dimensional long-range-ordered crystal. This crystallization occurs mainly in body centered cubic (bcc) or face centered cubic (fcc) lattices, depending on the diameter and on the density of the particles [3].

The lattice constant \(a\) is a well controlled parameter (for instance, by changing particle concentration) and the typical values are in the range \(a \approx 0.3-2 \mu m\). This is three or four orders of magnitude greater than in a usual solid crystal and as the interaction between two neighbouring particles is of the order of \(10 eV\), the elastic constants \(E\) are in the range \(E \approx 1-10^3 \text{ dyn/cm}^2\) [2]. This rough estimate is confirmed by the experimental results [4, 5, 6]. On the other hand, such a low value of the elastic modulus is very interesting for the study of the shear-induced melting since it is very easy to induce the flow of the CC [7-11].

The dynamical behaviour of colloidal crystals in absence of plastic motion is determined both by elasticity theory and hydrodynamics. Mitaku, Ohtsuki, Enari, Kishimoto and Okano [4, 8], soon followed by Joanny [12], were the first to write down linear equations of motion for CC. They wrote the equations of motion for the fluid and for the colloidal particles as classical dynamical equations. Their phenomenological description is a two fluid model. In that spirit the motion of the colloidal crystal is described by an equation of motion where the inertial terms of the particles were explicitly
introduced. The coupling between the colloidal particles and the fluid was introduced by a frictional force depending on their relative velocity. This phenomenological presentation has two limitations. First it only gives linearized equations and generalization to non linear regime may be not so simple and straightforward in such a phenomenological description. The second limitation is conceptual; in reference [4] the dynamical equation of the variable linked to the broken symmetry (crystallographic planes of the colloidal crystals) was not properly taken into account. The pertinent variable to describe a colloidal crystal is not the position of individual particles but a parameter taking into account the collective order. This last point was first noticed in a similar problem by Martin, Parodi, Pershan [13] who derived hydrodynamical equations for smectic liquid crystals. They pointed out that, for systems exhibiting spatial order, hydrodynamical modes are associated not only with conserved variables but also with the order parameter describing the broken symmetry. Indeed, when some symmetry can be continuously broken, the time evolution of the variable describing this broken symmetry is small and the variable is hydrodynamic. For colloidal crystals hydrodynamical variables will be associated either with conserved quantities (such as momentum density) or with the continuous broken symmetry i.e. crystallographic planes of the colloidal crystal. Then the equation of motion of colloidal particles does not arise from a classical dynamical equation as in reference [4] but is obtained by writing down a decay equation for the order parameter, the expression of which results from thermodynamic properties of the system. In this paper we shall first derive non linear equations of motion following the method introduced by Dzyaloshinskii and Volovick [1] (noted hereafter DV). They proposed a general shortcut method for deriving non linear equations. We shall use, as in the DV paper, a formalism based on hydrodynamic Poisson brackets. This yields the non linear equations of motion without dissipation as shown in section 2. Then in section 3, we include dissipation with use of the classical method of irreversible phenomena [14, 15]. The last section is devoted to an explicit expression of the equations of motion in a harmonic approximation of the elastic energy.

2. The equations of motion without dissipation.

Let us first recall the hydrodynamical equations describing the motion of colloidal crystal given in reference [4].

\[ n m \frac{\partial u_{el}}{\partial t} + n m_0 \frac{\partial v_{fl}}{\partial t} + n \zeta \left( \frac{\partial u_{el}}{\partial t} - v_{fl} \right) = G_{ij} \Delta u_{el} \quad (1a) \]

\[ \rho \frac{\partial v_{fl}}{\partial t} + n \zeta \left( v_{fl} - \frac{\partial u_{el}}{\partial t} \right) = \eta \Delta v_{fl} \quad (1b) \]

\[ \mathbf{u}_{el} \] is the displacement of the particles, \( \mathbf{v}_{fl} \) the velocity of the fluid, \( n \) is the number density, \( m \) and \( m_0 \) are the mass of a particle and the medium of the same volume, \( \rho \) its specific mass, and \( \zeta \) is the friction coefficient of a particle.

In this description both media are treated on the same footing. Equation (1a) describes the motion of the elastic medium, and equation (1b) the motion of the viscous fluid. They are coupled through the term \( n \zeta \left( \frac{\partial u_{el}}{\partial t} - v_{fl} \right) \) which is nothing else than the force acting on one sphere due to its relative motion through the fluid. Stokes' formula, which expresses the drag force exerted on a slow moving sphere of diameter \( d \) in a fluid of viscosity \( \eta_0 \) [16] is of the same form:

\[ F = 3 \pi d \eta_0 v \quad (2) \]

\( v \) is the relative velocity of the sphere with respect to the fluid.

Equations (1) which are linear only describe situations close to equilibrium. We first expect a non linear approach to introduce convective terms of the form \( (\mathbf{W} \cdot \nabla) \mathbf{u}_{el} \) or \( (\mathbf{W} \cdot \nabla) \mathbf{v}_{fl} \). The point is then to determine which velocity \( \mathbf{W} \) enters in both terms. Besides this clarification, the theory we present here leads to different hydrodynamical equations. Indeed our approach differs conceptually from the one of reference [4] but follows the theory given by Martin, Parodi and Pershan [13] and by DV [1]. Our analysis will reveal the difference of status between a variable which is conserved such as the momentum and the one which describes the broken symmetry (namely the position of crystallographic planes).

Let us now list the independent hydrodynamic variables for colloidal crystals:

\[ \rho_k \] momentum density \(^{(1)}\);

\[ \rho_{el} \] mass density of the elastic medium;

\[ \rho_{fl} \] mass density of the fluid;

\( s \) entropy density and

\[ \omega_k^a \] the vectors normal to the crystallographic planes

\[ X^\alpha (\alpha = 1, 2, 3) \]

\[ \omega_k^a = \frac{\partial X^\alpha}{\partial x_k} = \delta_k^a X^\alpha. \quad (3) \]

These vectors are vectors of the reciprocal Bravais lattice. Notice that the Latin indices \( i, j \ldots \) are used for the spatial coordinates in a fixed reference frame, while the Greek indices \( \alpha, \beta \ldots \) are related to the three axes linked to the crystal. The components of the inverse tensor \( \omega^{-1} \):

\[ \omega_k^a (\omega^{-1})_a^\alpha = \delta_k^\alpha \quad (4) \]

are vectors of the local Bravais lattice of the crystal.

If we neglect the defects [17], the \( X^\alpha \) are single-

\(^{(1)}\) \( \rho_k \) is the momentum density of the center of mass of a volume element of the system and not the momentum of each of the constituents.
valued coordinates and from (3) the \( \omega_k^a \) then satisfy the integrability condition:

\[
\partial_t \omega_k^a = \delta_{ik} X^a = \partial_k \omega_i^a.
\] (5)

In that case, one easily finds a relation between \( \omega_k^a \) and the usual elastic deformation \( u(x) \) of the lattice.

The unstrained state of the crystal is defined by:

\[
\delta_\omega^a_k = \frac{\partial X^a}{\partial x^k} = \partial_k X^a
\] (6)

corresponding to Bravais lattice vectors:

\[
\xi^a = (\omega^{-1})^a_k e_k.
\] (7)

Under deformation, the new Bravais lattice vectors are:

\[
e_a = \xi_a + (\omega^{-1})^a_k (\partial_k u^l) e_l
\] (8)

and the new normals read:

\[
\omega_k^a = \delta_\omega^a_l (\delta^i_{k} - \partial_k u^l)
\] (9)

with the above relations, the strain tensor of the linear theory becomes:

\[
e^l_k = \frac{1}{2} (\delta^l_{ik} + \delta^{l}_{ik} \partial_k \partial_l u^k)
\]

\[
= \delta^l_k - \frac{1}{2} \left[ (\omega^{-1})^a_k \omega_k^a + \delta^l_k (\omega^{-1})^a_k \omega_k^a \right].
\] (10)

With the above choice of hydrodynamic variables, the energy is given by:

\[
H = \int dV \varepsilon (p, \rho_B, \rho_{el}, s, \alpha_k^a).
\] (11)

Requiring the Galilean invariance of the energy density \( \varepsilon \) leads to the decomposition of \( \varepsilon \) in a kinetic and an internal part:

\[
\varepsilon = \frac{P^2}{2 \rho} + \bar{\varepsilon} (\rho_{el}, \rho_B, s, \omega_k^a) \quad \rho = \rho_{el} + \rho_B.
\] (12)

The equations of motion without dissipation given by DV [1] are then:

\[
\partial_t p_k = - \partial_l (v_l p_k) - \partial_k p - \partial_l (\sigma_l^a \omega_k^a)
\] (13)

\[
\partial_t \rho_A = - \partial_l (\rho_A v^l)
\] (14)

where \( \rho_A \) stands for both \( \rho_{el} \) and \( \rho_B \).

\[
\partial_t s = - \partial_l (s v^l)
\] (15)

\[
\partial_t \omega_k^a = - \partial_k (\omega_k^a v^l)
\] (16)

where one has used (12) to write \( \frac{\partial \varepsilon}{\partial p_k} = v^k \) as well as the definition:

\[
\sigma_l^a = - \frac{\partial}{\partial \omega_l^a}.
\] (17)

The scalar \( p \) in (13) is the usual pressure:

\[
p = - \varepsilon + p_1 v^l + Ts + \sum_A \rho_A \mu_A
\] (18)

so that one gets:

\[
\partial_t p = p_1 \partial_k v^l + \sum_A \rho_A \delta_k \mu_A + s \delta_k T - \sigma_l^a \partial_k \omega_l^a
\] (19)

where \( T = \frac{\partial \varepsilon}{\partial s} \) is the temperature and \( \mu_A = \frac{\partial \varepsilon}{\partial \rho_A} \) is related to the usual chemical potential of the \( A \) component \( \bar{\mu}_A = \frac{\partial \varepsilon}{\partial \rho_A} \) by the relation: \( \mu_A = \bar{\mu}_A - v^l / 2 \).

The tensor \( v^l p_k + \sigma_l^a \omega_k^a \) must be symmetric in \( l \) and \( k \) since the total angular momentum of our system is conserved in the absence of any external torque [15]. If it is not the case, it is always possible to define new \( \tilde{p}_k \) and \( \sigma_l^a \) in order to satisfy the symmetry property [13].

Equations (13-16) constitute a complete set of equations describing the dynamics of the CC in the absence of dissipation. There is very little change with respect to DV [1]: we have two equations for the mass densities since the CC are a two-component system and the definition of \( p_k \) is also modified.

3. The equations of motion with dissipation.

In the preceding section, we wrote down four kinetic equations for the variables \( p_k, \rho_A, s, \omega_k^a \) (Eqs. 13-16). The theory of irreversible processes allows us to rewrite (13-16) with dissipative terms. Notice however that we are looking first of all for a set of equations able to generalize the linear equations of motion for CC to treat non linear situations. As a consequence, we shall mainly focus our attention on equation (13) for \( p_k \) and (16) for \( \omega_k^a \). On the other hand equations (14, 15) cannot be omitted so that we shall also consider their dissipation terms.

In order to get these dissipative terms, we shall follow the standard procedure in use in the theory of irreversible phenomena [14, 15]. This method is based on two main assumptions:

- it is possible to define local thermodynamic quantities having the same relations between them as the ones for the thermodynamic variables defined at equilibrium;
- there is a positive local entropy source.

With these two assumptions, it is possible to identify the dissipative terms and to give their explicit form.
Let us write again the equations of motion (13-16) including the unknown dissipative terms:

\[ \partial_t p_A + \partial_i (p_A v^i) = \partial_i \sigma^{ij}_k \]  

(20)

where \( \sigma_k^{ij} = \sigma_k^{ij} - \sigma^{ij}_a \omega^a_k - p \delta_k^{ij} \) is the total stress tensor and \( \sigma^{ij}_k \) is the unknown dissipative part.

The continuity equation for the mass densities are:

\[ \partial_t \rho_A + \partial_i (\rho_A v^i_A) = - \partial_i j_A^i \]  

(21)

As usual, one gets the form of the diffusion current \( j_A^i \) by writing a conservation equation for each of the constituents, in the absence of any chemical reactions:

\[ \partial_t \rho_A + \partial_i (\rho_A v^i_A) = 0 \]  

(22)

The diffusion currents then become:

\[ j_A^i = \rho_A (v^i_A - v^i) \]  

(23)

where \( v^i_A \) is the mean velocity of the \( A \) component in a volume element while \( v^i \) is the center of mass velocity of this volume. By definition, we have

\[ \sum_A \rho_A v^i = \sum_A \rho_A v^i_A \]  

with the consequences:

\[ \sum_A j_A^i = 0 \quad \text{and} \quad \partial_t \rho + \partial_i (\rho v^i) = 0 \]  

(24)

This last relation implies the conservation of the total mass of the system. The continuity equation for the entropy is written as:

\[ \partial_t s + \partial_i (sv^i) = - \partial_i j_s^i + i \]  

(25)

where \( j_s^i \) is the entropy flux and \( i \) its source, often called irreversibility, with \( i \geq 0 \) according to the second principle of thermodynamics. The last continuity equation for the vectors \( \omega^a_k \) (describing the lattice deformations) is written as:

\[ \partial_t \omega_k^a + \partial_k (\omega^a_k v^i) = - \partial_k j_k^a \]  

(26)

The continuity equation for the energy density \( \varepsilon \) is:

\[ \partial_t \varepsilon + \partial_k (\varepsilon v^k - \sigma_k^{ij} v^i + j_k^i) = 0 \]  

(27)

where \( \varepsilon v^k \) is the convective part of the energy flux.

The other part has two contributions:

\[ \sigma_k^{ij} v^i, \quad \text{the density of work current due to the surface strains and volume forces;} \]

\[ j_k^i, \quad \text{the energy flux from other sources of thermal or chemical nature.} \]

Introduction of equations (20, 21, 25, 26) in the continuity equation (27) allows for the identification of the dissipative terms.

\[ \partial_t \varepsilon + \partial_k (\varepsilon v^k - \sigma_k^{ij} v^i + j_k^i) = \sum_A \mu_A \partial_t \rho_A - \frac{v^2}{2} \partial_t \rho + v^i \partial_i \rho + T \partial_t s + \]

\[ + \sigma_a^i \partial_i \omega^a_k + \partial_k (\varepsilon v^k - \sigma_k^{ij} v^i + j_k^i) = - (\omega^a_k \sigma_a^i + p \delta_k^{ij} + \sigma_k^{ij}) \partial_i \rho^k + \]

\[ + T - j_k^i \partial_k j_k^i - \sum_A \mu_A \partial_t j_A^i - \sigma_a^i \partial_i j_a^i + \partial j_s^i = 0 \]  

(28)

where we have used the thermodynamical relation \( \varepsilon = Ts + \sum_A \rho_A \mu_A - p \). One first identifies the current:

\[ j_A^i = T j_A^i + \sum_A \mu_A j_A^i + \sigma_a^i j_a^i. \]  

(29)

Then, with the definition (20) of \( \sigma_k^{ij} = \sigma_k^{ij} \) and with \( v_k^i = \frac{1}{2} (\partial_i v^k + \delta^k \partial_i v) \partial_j p \) one rewrites the irreversibility in the following form:

\[ i = \frac{1}{T} [\sigma_k^{ij} v_k^i - j_k^i \partial_i T - \]

\[ - \sum A j_A^i \partial_i \mu_A - j_a^i \partial_a \sigma_a^i] \]  

(30)

It is convenient here to decompose a second order symmetric tensor \( \sigma_k^{ij} \) into a traceless tensor \( \sigma_k^{ij} \) and a diagonal tensor \( 1/3 \sigma_k^i \delta_k^i \), where \( \sigma_k^i \) is the trace of \( \sigma_k^{ij} \). The relation (30) then becomes:

\[ \sigma_k^{ij} = 2 \eta_k^{ij} v_k^i. \]  

(32)

From the positivity of \( i \), one finds the relations between the known thermodynamic forces \( v_k^i, - \partial_i T, - \partial_i (\mu_{el} - \mu_{el}), - \partial_i \sigma_a^i, 1/3 v_k^i \) and the unknown thermodynamic currents \( (\delta_k^i, j_k^i, j_k^i, j_a^i, \sigma_k^{ij}). \) Following the results given in appendix, one finds:

\[ \sigma_k^{ij} = 2 \eta_k^{ij} v_k^i. \]  

When the reference frame axis coincides with the cubic cell axis of the CC, the anisotropic viscosity tensor \( \eta_k^{ij} \) has the symmetry properties (A.5) and the non-vanishing components are:

\[ \eta_k^{ij} = \eta_1, \quad i, j = 1, 2, 3 \]

\[ \eta_k^{ij} = \eta_2 = - \eta_1 / 2, \quad i \neq j \]  

(33)

\[ \eta_k^{ij} = 1/2 \eta_3, \quad i \neq j. \]
with (33), the relation (32) becomes

\[ \sigma_{ij} = 3 \eta_1 (\delta_i \delta_j) - \eta_1 \text{div} \mathbf{v} \] (without summation)

= 2 \eta_1 \text{div} \mathbf{v} \tag{34a}

\[ \sigma_{ij} = 2 \eta_3 v_i v_j \] (34b)

For the vectorial terms of (31), one gets

\[ j^a = L_{a b} (- \delta_i \phi \delta_j T) + L_{a c} (- \delta_i \phi \delta_j (\mu_{el} - \mu_n)) \]

\[ j^a = L_{a c} (- \delta_i \phi \delta_j T) + L_{a c} (- \delta_i \phi \delta_j (\mu_{el} - \mu_n)) \] (35)

where from Onsager's relations [16], \( L_{a c} = L_{c a} \). These coefficients are responsible for the Soret and Dufour effects. We expect the corresponding terms to have little influence on the motion so that we neglect them. \( L_{a c} \) and \( L_{c a} \) are the usual thermal conductivity and the diffusion coefficients. For our purpose, the scalar terms of (31) are more interesting

\[ j^a = L_{a b}^2 (- \delta_i \sigma_{ij}) + L_{a b} v_k v_i \]

\[ \sigma_{ij} = L_{a b}^2 (- \delta_i \sigma_{ij}) + L_{a b} v_k v_i \] (36)

since \( j^a \) is a scalar in the spatial coordinates denoted by Latin indices. The cubic symmetry of the crystal implies:

\[ L^a = L^a = 0 \]

\[ L^a = L^a = 0 \]

\[ L^a = L^a = 0 \]

\[ L^a = L^a = 0 \]

\[ L^a = L^a = 0 \]

\[ L_i = 3 \xi \] .

Using (37), one writes (36) as:

\[ j^a = - \delta_i \sigma_{ij} \]

\[ \sigma_{ij} = 3 \xi \text{div} \mathbf{v} \] (38)

The scalar \( \xi \) is the bulk viscosity [16] while the meaning of \( \lambda \) will appear in the next section.

With the relations (34, 35, 36), the irreversibility (31) can be written explicitly in the form

\[ i = \frac{1}{T} \left[ 3 \eta_1 \sum_i (\partial_i v_i)^2 + \eta_3 \sum_i (v_i v_i) + \frac{L_{a c}}{2} \text{grad} T^2 ight. \]

\[ + 2 L_{a c} \text{grad} T \text{grad} (\mu_{el} - \mu_n) \]

\[ + L_{a c} \text{grad}^2 (\mu_{el} - \mu_n) \]

\[ + \frac{1}{\lambda} \sum_a (\delta_i \sigma_{ij}^a) + (\xi - \eta_1) \text{div} \mathbf{v} \right] \]

and the power dissipated in any dynamical phenomenon is:

\[ P = \int dV i T \].

The entropy production \( i \) is positive if one imposes the necessary conditions:

\[ 2 \eta_1 + \xi > 0 \]

\[ \eta_3 > 0 \]

\[ L_{a c} > 0 \]

\[ L_{a c} > 0 \]

\[ \lambda > 0 \] (40)

and the sufficient conditions

\[ \eta_1 > 0 \]

\[ \xi > \eta_1 \] (41)

4. The equations of motion for colloidal crystals in the harmonic approximation.

The expressions of the dissipative terms (34) and (38) can be introduced in the equations of motion (20) and (26). One then has a complete set of nonlinear equations describing the dynamics of CC. In this section, we give the form of these equations under the following assumptions:

- we limit ourselves to the harmonic approximation of the elastic energy \( e_{el} \) [18]

\[ e_{el} = 1/2 K^{lm}_h e_k e_m \] (42)

- we consider all transport coefficients or elastic moduli as being constant.

In equation (42) the strain tensor is given by (10) and the tensor \( K^{lm}_h \) of the anisotropic elastic modulus has the symmetry properties (A.5):

\[ K_{ii} = C_{11}, K_{ij} = C_{12}, i, j = 1, 2, 3 \]

\[ K_{ij} = C_{12} = C_{ij} \]

\[ K_{ij} = K_{ij} = K_{ij} = C_{44}, K_{3}, i \neq j \] (43)

Introducing (10) and (42) in the definition (17) of \( \sigma_{ij} \), one writes:

\[ \sigma_{ij} = \frac{\partial e_{el}}{\partial \omega_{ij}} = \frac{\partial e_{el}}{\partial \omega_{ij}} \]

\[ = -K^{lm}_h e_k e_m (\delta_{ij} - \frac{1}{3}) \] (44)

and in the harmonic approximation, it is convenient to write

\[ \sum_{ij} \omega_{ij} \sigma_{ij} = \sum_{ij} \delta_{ij} \sigma_{ij} = -K^{lm}_h e_k e_m \] (45)

With (34, 38 and 45), the equation of motion for the momentum density (13) finally becomes

\[ \rho (\partial_t v_k + v^j \partial_j v_k) = - \partial_i \rho + (3 \eta_1 - 2 \eta_3) \delta_k^j v_k + \xi - \eta_1 \text{div} \mathbf{v} \] (46)

With (35), and for isothermal displacements, the equations of motion for the mass densities are:

\[ \partial_t \rho_{cl} + \partial_i (\rho_{cl} v^i) = L_{cc} \Delta (\mu_{el} - \mu_n) \]

\[ \partial_t \rho_n + \partial_i (\rho_n v^i) = -L_{cc} \Delta (\mu_{el} - \mu_n) \] (47)
These equations express the diffusion of the constituents under the action of a chemical potential gradient. These two relations lead to the continuity equation for the mass density $\rho$ of the system:

$$\partial_t \rho + \partial_i (\rho v^i) = 0 . \tag{48}$$

Similarly, one finds for the entropy density:

$$\partial_s + \partial_i (sv^i) = L_{\infty} \Delta (\mu_{cl} - \mu_0) + i . \tag{49}$$

With the use of (38), one obtains the equation for the vector $\omega_0^a$:

$$\partial_t \omega_0^a + \partial_i (\omega_0^a v^i) = - \partial_{jk} \alpha = \frac{1}{\lambda} \delta^{\alpha\beta} \partial_k \partial_j \sigma_{\beta}^j . \tag{50}$$

In the linear approximation, $\omega_0^a v^i \approx \omega \alpha \alpha^i v^i$, the equation (50) takes the form:

$$- \partial_i \partial_{jk} \partial_k u^j + \partial_r (\partial_j^a v^j) = \frac{1}{\lambda} \delta^{\alpha\beta} \partial_k \partial_j (K_{ij} \epsilon_{m} \epsilon_{m} (\omega_0^j \partial^j \alpha)^i ) . \tag{51}$$

Multiplying by $\omega_0^{-1} \partial_k$ and integrating with respect to $x^k$, one finally gets:

$$\lambda (\partial_i u^i - v^i) = \delta^{ij} K_{ij} \epsilon_{m} \epsilon_{m} \tag{52}$$

or, explicitly,

$$\lambda (\partial_i u^i - v^i) = (K_1 - K_2 - 2 K_3) \partial_j^i u^j + (K_2 + K_3) \partial_j \text{div} u + K_3 \Delta u_j . \tag{53}$$

Notice that in the above equation, the Einstein implicit convention of summation is not used for the term $\partial_j^i u^j$.

From the above relation, the interpretation of $\lambda$ is obvious. It expresses the resistance of the medium to the permeation, i.e. to the relative motion of the fluid and of the elastic medium. The coefficient $\lambda$ is the permeation coefficient by unit volume and for a density of particles $\pi = 1/a^3$, its order of magnitude can be found with use of Stokes’ formula (2):

$$\lambda \approx 3 \pi d \eta \epsilon a^3 \approx 10^7 g \text{ cm}^{-1} \text{ s}^{-1} \tag{54}$$

for typical values of $d$ (0.1-0.6 $\mu$m), $\epsilon$ (0.3-2 $\mu$m) and $\eta$, the effective viscosity of the suspension ($\approx 0.1 g \text{ cm}^{-1} \text{ s}^{-1} = 0.1 \rho$ [6]).

The viscosity introduced in (54) is the one of the complete suspension and not only the viscosity of the solvent. This effective viscosity includes the collective hydrodynamic effects due to a density of particles in the suspension as well as the effects of the electric interaction between the particles.

Equation (53) is very reminiscent of the classical permeation equation in smectic phases [19]. It specifies the motion of the fluid relative to the ordered structure and indicates explicitly that inertial terms, as introduced in equation (1a) are irrelevant. Relations (46, 48, 50) are the fundamental set of hydrodynamical equations of the colloidal structure. For slow motions, their linearized expressions lead to the same modes as those obtained from equations (1a) and (1b) where the inertial terms are neglected [4, 5, 12].

5. Conclusion.

In this paper, we have derived general hydrodynamical equations for colloidal crystals. This theory describes hydrodynamic modes i.e. long-lived modes related to conserved variables as well as to continuous broken symmetry. We obtain equations of motion very reminiscent of those for smectic liquid crystals. For instance the hydrodynamic description reveals a permeation motion similar to the smectic one. This mode is characteristic of the motion of the crystalline planes relative to the ambient fluid. Our description is quite general, non linear and differs conceptually from linearized phenomenological equations previously introduced [4].

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Appendix.

The relation (31) may be written in the general form

$$i = 1/T J^i X_i \tag{A.1}$$

where $X_i$ are the known thermodynamic forces and $J_i$ are the unknown thermodynamic currents. From the second thermodynamic principle, one must have $i \geq 0$. This condition will be satisfied if one constructs a quadratic form in $X_i$ by defining:

$$J^i = L^i_{ij} X_j \tag{A.2}$$

where the $L_{ij}$ are phenomenological constants having the symmetry of the system. Let us write (A.1) in a more precise form in which the tensorial nature of the various terms appears explicitly (see (31)):

$$i = J^i_{ij} X^k X^j + J^i \partial_i X + JX . \tag{A.3}$$

Following the analysis of de Groot and Mazur [15] for a system having a cubic symmetry, this leads to the well known results:

$$J^k = a^k_{ij} X^j$$

$$J^k = b^k_{ij} X^j$$

$$J = c X \tag{A.4}$$
where the 4th order tensor $a_{klji}$ has the obvious symmetry

$$a_{klji}^{kl} = a_{klji}^{lj} = a_{klji}^{ki}$$

and the non-vanishing components:

$$a_{ij}^{ij} = a_1, \quad r, s = 1, 2, 3$$
$$a_{ij}^{rs} = a_2, \quad r \neq s$$
$$a_{ij}^{ss} = a_3$$  \hspace{1cm} (A.5)

Moreover

$$\sum_i a_{ij}^{kl} a_{klji} = a_1 + 2a_2 = 0 \quad \text{since} \quad J' = 0.$$  

We observe in (A.4) that the non-negativity of $i$ is imposed separately to each term of (A.3) and that the currents and thermodynamic forces of different tensorial character do not couple. This result, known as the Curie principle, is a consequence of our assumption according to which the $L_{\alpha\beta}$ are constant.

References