Shear waves in colloidal crystals: I. Determination of the elastic modulus

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Shear waves in colloidal crystals : I. Determination of the elastic modulus

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Résumé. — On induit des ondes de cisaillement dans un échantillon de latex. La détection des vibrations excitées se fait par une technique de diffusion de la lumière (anneaux de Kossel). L'amplitude de vibration de l'échantillon dépend de la fréquence. Il apparait une série de résonances dont l'analyse permet de déterminer le module élastique de l'échantillon. On étudie la variation de ce module en fonction de différents paramètres caractéristiques du latex.

Abstract. — Shear waves are excited in a latex sample. One detects the vibrations of the sample using light scattering phenomena (Kossel rings). The amplitude of vibrations of the latex sample, when recorded as a function of the frequency of excitation, presents a series of resonances. Analysis of the resonance peaks allows to determine the elastic modulus of the latex crystal. We study the variation of the elastic modulus as a function of different parameters characteristic of the latex.

1. Introduction. — Polymer colloids are two component systems. They are made of :

(1) polymeric spheres, few tenth of micrometers in diameter, dispersed in the solvent at concentration \( n = 10^{12} \) to \( 10^{13} \) particles/cm\(^3\);

(2) a solvent such as water characterized by the viscosity \( \eta \).

From the existence of the selective light diffraction it has been concluded that under appropriate conditions the polymeric spheres are ordered in a tridimensional crystal. Numerous articles are related to the phenomena of the light Bragg diffraction [1, 2, 3] and to the fundamental problem of crystallization under the action of repulsive electrostatic interactions [4-7]. This last problem rests on the knowledge of the interaction forces which, in principle, can be deduced from the elastic modulus of the crystal. In spite of this fact only very few articles report the measurements of mechanical properties of the colloid crystals.

The first estimate of the elastic modulus \( E \) has been performed by Mitaku et al. [8] using the torsional crystal method. Due to the relatively high excitation frequency (40 kHz and 70 kHz) they interpret the result \( E \approx 10^3 \) dyn/cm\(^2\) as being probably indicative only of short range ordering. In fact, in the disordered (liquid) phase obtained by addition of KCl salt (at \( 10^{-4} \) N concentration) they measured a finite elastic modulus smaller by a factor of two as compared with the result obtained in the ordered phase.

In another experiment performed with a Zimm low shear viscometer Mitaku et al. measured the yield stress of about 0.5 dyn/cm\(^2\). Using the relation which relates the yield stress to the elastic modulus they find the value of elastic modulus compatible with that obtained by torsional quartz methods.

Independently, Crandall and Williams [9] estimated the static rigidity from the elastic deformation of a crystalline column under the earth gravitational field. They obtained a value of \( \approx 1 \) dyn/cm\(^2\) for a latex containing \( 10^{12}-10^{13} \) particles/cm\(^3\). Although very simple, this method would be difficult to use systematically to measure the elastic modulus because of a prohibitively long time of sedimentation required to attain the equilibrium deformation.

In this article we propose a method which allows to determine simply and accurately the elastic modulus of the colloid crystals from the spectrum of their mechanical vibrations. In section 2 we describe the method and the experimental set-up which is used :

(1) to excite shear waves in a sample contained in a test tube ;
(2) to detect the amplitude and phase of these vibrations using the light diffraction phenomena.

The amplitude of vibrations of the latex sample when recorded as a function of the excitation frequency (Section 3) presents a series of resonance peaks which corresponds to the formation of the standing waves. Such a spectrum is indicative of the elastic modulus (in general complex with the viscous damping factor represented by the imaginary part) of the latex sample as it is shown in section 4 where we analyze theoretically the problem of shear waves in ordered latexes. The phase and amplitude of the shear waves in cylindrical geometry are calculated in particular. Preliminary measurements of the elastic modulus as a function of polymer particles concentration as well as a function of NaOH concentration (introduced progressively) are presented in section 5.

2. Experiments. — 2.1 Mechanical set-up. — The latex sample is contained in a glass test tube T of internal diameter of 14.3 mm and of 150 mm length. In order to excite the shear waves, the test tube is forced to oscillate around its axis z using a system represented in figure 1. The test tube T holds on the metallic cylinder C by friction. Being suspended on ball bearings B, the cylinder and the test tube have only one degree of freedom; they can rotate around the z axis. They are coupled to the loudspeaker membrane through a rigid rod R and by this means the small amplitude oscillations of the test tube can be produced. The oscillation amplitude \( \varphi_0 \) was measured as a function of the frequency. It has been found that the mechanical resonance of the loudspeaker, loaded by the mass of moving parts in the system, is situated at 35 Hz. Consequently in the range of frequencies between \( f_{\text{min}} = 0 \) Hz and \( f_{\text{max}} = 40 \) Hz the resonances detected by the apparatus (as those shown in Fig. 5) are due to the colloidal crystals sample.

The largest elastic modulus values \( E_{\text{max}} \) which can be measured with the operating range 0-40 Hz can be estimated as follows: the fundamental standing shear wave in a cylinder of diameter \( 2R = 14.3 \) mm has a frequency (calculated in section 4, form. (4.19))

\[
    f_0 \approx \frac{1}{2R} \left( \frac{E}{\rho} \right)^{1/2}
\]

From the condition that this frequency cannot be larger than \( f_{\text{max}} \) one finds that

\[
    E_{\text{max}} = \rho \frac{4}{R^2} f_{\text{max}}^2 = 2500 \text{ dyn/cm}^2.
\]

The largest elastic modulus we measured, up to now, in ordered latexes was of about 110 dyn/cm². So that not only the fundamental mode but also a few harmonics were observed.

2.2 Shear wave detection. — A 20 mW HeNe laser beam is focused on a small area of the latex sample. The test tube containing the sample is immersed in a spherical vessel (10 cm in diameter) filled with water so that the incident and outgoing rays propagate practically without refraction. The spherical vessel is covered by a nylon sock NS which acts as a translucent screen for the backscattered light. The diffraction image characteristic of the crystalline structure observed on the screen is composed of:

(i) Bragg diffraction spots;
(ii) Kossel lines (KL in Figs. 1 and 2);
(iii) diffuse background light scattering.

Kossel lines allow one to determine the crystallographic structure very simply (easier than specular reflexion spots) because their configuration does not depend on the incident beam direction. A Kossel line is in fact an intersection of the Kossel cone with the screen surface (Fig. 2). Each Kossel cone is centered around the normal \( \mathbf{n} \) to the corresponding refracting crystallographic planes. The cone angle \( \theta \) is indicative of the interplanar spacing \( d \). On the spherical screen surface the Kossel lines are circular (Kossel rings). Their configuration is indicative of the crystalline structure; while their diameters provide an infor-
Fig. 2. — Detection of the Kossel line motion.

formation about the interplanar spacing (see Fig. 2). When the crystal is deformed by the shear wave the diameter and the position of the Kossel rings change.

In order to detect this motion a photodiode with a large photosensitive surface was situated near to the screen in such a way that only half of the photosensitive area is observed by the Kossel ring (Fig. 2). When, due to the crystal deformation, the Kossel ring moves the observed area changes and the total light intensity is modulated.

It is also possible to detect the deformation using Bragg spots and even background light scattering. In this last case the largest signal was observed when the incident angle corresponds to assumed Bragg reflexion condition. The signal delivered by the photodiode is amplified by an AC stage. In order to detect the amplitude the AC signal \( I(f) \) is multiplied by itself \( (I(f)I(f)) \) using a four quadrant analog multiplier and then the average value \( I(f)^2 \) is obtained by filtering using an R.C. low pass filter. The filter time constant \( \tau_0 \) was 3 s.

The information about the phase of the crystal deformation is obtained by multiplying \( I(f) \) by an AC reference voltage \( V_r(f) \) of constant amplitude in phase with the loudspeakers supply voltage and filtering. The \( I(f)^2 \) and \( I(f)V(f) \) signals are plotted as a function of the frequency on a XY recorder. The VCO input voltage is applied to the X input.

2.3 FREQUENCY SWEEP. — The loudspeaker is supplied from a voltage controlled oscillator (VCO in Fig. 3). Due to the low operating frequencies the sweep rate \( \frac{df}{dt} \) must be low enough in order to obtain a good resolution \( \Delta f_{\text{res}} \) in the response spectrum. \( \Delta f_{\text{res}} \) can be estimated to be of the order of \( 1/\Delta f_{1/2} \) where \( \Delta f_{1/2} \) is the halfwidth of the resonance peaks. It has been observed experimentally (section 4) that \( \Delta f_{1/2} \) can be as small as 0.3 Hz. The filter time constant \( \tau_{\text{def}} \) has been chosen to be 3 s. We conclude that in order to obtain a resolution \( \Delta f_{\text{res}} \) of 0.3 Hz it is necessary to use the sweep rate lower than

\[
\frac{\Delta f_{\text{res}}}{\tau} \approx 10^{-1} \text{ Hz/s}.
\]

Such a slow sweep control signal \( V_{sw} \) was obtained easily using a microprocessor driven 12 bit digital to analog converter. The microprocessor program developed for this purpose offers to the user the following functions:

a) a choice of the start and stop frequencies,

b) a choice of the sweep rate and sense,

c) a possibility to stop the sweep at a particular frequency and resume the sweep from this frequency at a later time.

3. Results. — 3.1 SAMPLE PREPARATION AND CHARACTERIZATION OF THEIR CRYSTALLOGRAPHIC STRUCTURE. — Two different latex samples have been prepared and investigated in our laboratory: Sample A was made of polystyrene spheres with diameter of the order 1 000 Å dispersed in water. After purification, using the ionic exchange resin (Amberlite MB-3) the latex was introduced in the test tube (see Fig. 1); about 1/3 of the total height of the tube was filled by the latex sample.

The test tube was then located in the spherical vessel in such a way that the small area of the sample, illuminated by the laser beam, coincided with the spherical vessel center O. The global configuration of Kossel rings suggested that the crystallites which are in contact with the glass wall have the BCC structure with the (110) planes parallel to the interface. From the interplanar spacing \( d_{110}^{\text{BCC}} = 0.247 \mu m \) the polystyrene spheres concentration was determined as follows:

\[
n_{\text{BCC}} = \frac{0.7071}{d_{110}^{2}} = 4.7 \times 10^{13} \text{ sph./cm}^3.
\]
Sample B was made of spheres with diameter of order 2,000 Å. As deduced from the light diffraction image this sample was polycrystalline with the cubic structure as well. The crystallites which were in contact with the glass walls had FCC structure with their (111) planes parallel to the interface. The numerical density of the polymeric particles as calculated from the interplanar distance $d_{111}^{\text{FCC}} = 0.40 \mu m$ was

$$n_{\text{FCC}} = \frac{0.77}{d_{111}^{\text{FCC}}} = 1.2 \times 10^{13} \text{ part/cm}^3$$

The sample B was diluted progressively by addition of a known volume of distilled water. After each dilution the sample was purified with the ionic exchange resin. The crystalline ordering was then recovered for density as low as

$$n = 1.5 \times 10^{12} \text{ part/cm}^3.$$  

3.2 Shear deformation. — The behaviour of the latex sample depended strongly on the excitation amplitude. For the oscillation amplitude small enough the crystallite deformation was elastic; the Kossel ring oscillations were proportional to the excitation amplitude and the global configuration of the diffraction image was conserved in average. On the contrary, for the excitation large enough the plastic crystal deformation was observed: the diffraction image was destroyed. When the excitation was removed a new Kossel rings configuration appeared.

In general, the samples were first submitted to a plastic shear deformation in order to improve the crystallographic structure of the sample. Then the measurements of the amplitude and phase of the elastic oscillations were made using the method described in the previous section.

In figure 4 we present a typical plot of $I^2(f)$ obtained with the sample A. It shows a series of peaks which indicates the mechanical resonances.

The spectrum $I^2(f)$ obtained with the sample B (Fig. 5) shows as well the resonance peaks but its general aspect is more regular.

4. Theoretical calculation of shear modes. — 4.1 Equations of motion. — The driven oscillations of the test tube induce shear waves in the latex sample. The latex sample is not a monocrystal but contains many microcrystallites with a dimension of the order of 10-few 100 µm. From an elastic point of view the sample will behave as an isotropic medium and as long as we are concerned with transverse modes it will be characterized by only one elastic modulus $E$.

In this section we shall first determine the shear modes induced by the test tube motion and then compute the resulting deformation on a crystallite close to the test tube surface. From a hydrodynamic point of view the medium is described by a two-component system (particles and fluid) [10, 11]. A first equation describes the latex sphere motion:

$$nm \frac{\partial^2 s}{\partial t^2} = nm \frac{\partial v}{\partial t} + n \xi_0 \left( v - \frac{\partial s}{\partial t} \right) + E \Delta s$$  

(4.1)

where $\Delta$ is the Laplacian operator, $n$ is the number density of particles, $m$ is the mass of the particles, $m_0$ is the mass of the solvent having the same volume as a particle, $\xi_0$ is the frictional coefficient of a particle, $s$ denotes the position of the particles and $v$ is the fluid velocity.

The term $nm \frac{\partial v}{\partial t}$ is similar to the Archimede force: it characterizes the force exerted (in absence of friction) by the accelerated fluid on a particle. The term $n \xi_0 \left( \frac{\partial s}{\partial t} - v \right)$ describes the friction between the particles and the fluid. The last term $E \Delta s$ represents the elastic force due to the fact that the particle is not isolated but belongs to an ordered suspension.
The fluid is well described by the Navier and Stokes equation with the additional term corresponding to the frictional force. This reads:

\[ \rho \frac{\partial \mathbf{v}}{\partial t} = -n \xi_0 \left( \frac{\partial \mathbf{v}}{\partial t} - \mathbf{v} \right) + \eta \Delta \mathbf{v} \quad (4.2) \]

where \( \eta \) is the medium viscosity.

The friction coefficient \( \xi_0 \) is of order \( 6 \pi \eta a_0 \) where \( a_0 \) is the particle radius. For particles with \( a_0 \sim 10^{-5} \text{ CGS} \), \( \xi_0 \) is typically of order \( 10^{-5} \text{ CGS} \) if \( \eta \sim 10^{-1} \text{ CGS} \).

The pressure does not appear in equation (4.2) since we are considering transverse modes. The first two terms of equation (4.1) are negligible compared to the friction terms since

\[ \frac{m_0 \xi_0}{\xi_0} \approx \frac{m_0 \xi_0}{\xi_0} \ll 1 \]

for the frequencies under use (\( f \) in the range 0-40 Hz). Then equation (4.1) reduces to:

\[ n \xi_0 \left( \mathbf{v} - \frac{\partial \mathbf{s}}{\partial t} \right) + E \Delta \mathbf{s} = 0. \quad (4.3) \]

Using equations (4.2) and (4.3) one can eliminate the velocity \( \mathbf{v} \), one obtains:

\[ \rho \frac{\partial^2 \mathbf{s}}{\partial t^2} - \left( \eta + \frac{\rho E}{\xi} \right) \frac{\partial \mathbf{s}}{\partial t} - E \Delta \mathbf{s} + \frac{\eta E}{\xi} \Delta^2 \mathbf{s} = 0 \quad (4.4) \]

where \( \xi = n \xi_0 \) is of order \( 10^7 \) to \( 10^8 \) CGS for samples with \( n \approx 10^{12}-10^{13} \). The second term of equation (4.4) reduces to \( \frac{\eta E}{\xi} \Delta^2 \mathbf{s} \) since \( \frac{\rho E}{\xi_0} \ll 1 \) (strong friction between the spheres and the solvent compared to the elasticity).

Let us show that the last term of equation (4.4) can be omitted since it would correspond to a mode with a very small penetration depth. As indicated in (Ref. (9), Eq. (4.4)) leads, for modes of the form \( \mathbf{s} = s_0 e^{i\omega t - k \eta} \), to the two (+ and -) dispersion relations:

\[ k_+^2 = \frac{\rho \omega^2}{E \left( 1 + \frac{i \eta}{\xi} \right)} \quad (4.6) \]

\[ k_-^2 = -\frac{\xi}{\eta} \left( 1 + \frac{i \eta}{E} \right) \quad (4.7) \]

The mode defined by \( k_- \) corresponds to a penetration depth \( \delta \) which is of the order of the distance between the spheres.

Indeed one gets

\[ \delta = \left( \frac{\eta E}{\xi} \right)^{1/2} \approx \left( \frac{1}{6 \pi \eta a_0} \right)^{1/2} \approx \left( \frac{d}{a_0} \right)^{1/2} d \sim d. \]

Such a mode with a penetration depth of the order of the distance between the particles will not contribute to the response of the whole sample. Then the term \( \frac{\eta E}{\xi} \Delta^2 \mathbf{s} \) can be omitted in equation (4.4) which now reads:

\[ \rho \frac{\partial^2 \mathbf{s}}{\partial t^2} - \eta \frac{\partial \mathbf{s}}{\partial t} - E \Delta \mathbf{s} = 0 \quad (4.8) \]

and corresponds to the dispersion relation (4.6).

Let us note that equation (4.8) takes into account the fact that the friction term \( n \xi_0 \left( \mathbf{v} - \frac{\partial \mathbf{s}}{\partial t} \right) \) expressed as \( -E \Delta \mathbf{s} \) (from Eq. (4.3)) is of the same order as the friction term \( \eta \Delta \mathbf{v} \) of equation (4.2).

### 4.2 Transverse Modes in the Cylindrical Geometry

As a first approximation one can consider that the particles move with the same velocity as the fluid:

\[ \frac{\partial \mathbf{s}}{\partial t} \approx \mathbf{v}. \quad (4.9) \]

The driven oscillations are imposed by a motion of the test tube of the form:

\[ T_\phi = A_0 e^{i \omega t} \quad (4.10) \]

where \( T_\phi \) is the tangential component (in cylindrical coordinates) of the test tube displacement (see Fig. 6).

Since the driven oscillations are tangential, one considers transverse modes of the form (in cylindrical coordinates):

\[ s_\phi(r, t) = s(r) e^{i \omega t} \quad (4.11) \]

In this description we omit the \( z \)-dependence of the modes since we are dealing with samples where \( R/H \ll 1 \) (\( H \) is the height of the sample). After some algebra equation (4.8) reads:

\[ \frac{d^2 s}{dr^2} + \frac{1}{r} \frac{ds}{dr} + \left( 1 - \frac{1}{r^2} \right) s = 0 \quad (4.12) \]
where \( y = k_+ r \) is a complex number and \( k_+ \) is defined by equation (4.6). In the following we shall write \( k \) instead of \( k_+ \).

On the surface of the test tube the fluid velocity must be equal to the velocity of the test tube:

\[
v_\varphi(R, t) = i\omega T_\varphi.
\]  

(4.13)

The boundary condition on the displacement \( s \) is deduced from equation (4.13) with use of equations (4.9), (4.10) and (4.11)

\[
s_\varphi(R, t) = T_\varphi \quad \text{or} \quad s(R) = A_0.
\]  

(4.14)

General solutions of equation (4.12) are Bessel functions of order one. Solution of equation (4.12), with boundary conditions (4.14) reads:

\[
s_\varphi = A_0 \frac{J_1(kr)}{J_1(kR)} e^{i\omega t}.
\]  

(4.15)

This corresponds to a fluid velocity

\[
v_\varphi = A_0 k\omega \frac{J_1(kr)}{J_1(kR)}.
\]  

(4.16)

The light diffraction is performed on a crystallite which is quenched with a specific crystallographic plane parallel to the cylindrical surface of the test tube (the choice of this plane and its orientation depend of course on the crystallographic structure of the sample). As a consequence, the geometrical structure of the Kossel lines strongly depends on the displacement \( s_\varphi \) and on the distortion \( \partial s_\varphi / \partial r \) of the latex crystallite in the immediate neighborhood of the test tube. In a newt paper we shall give the explicit relation between the shape of the Kossel lines and the applied excitations. Here we shall restrict our attention to the position of the mechanical resonances which correspond to the peaks of the local strain.

The local strain, obtained by differentiation of equation (4.15) and evaluated at \( r = R \) where the light diffraction occurs, reads:

\[
\frac{ds_\varphi}{dr} \bigg|_{r=R} = \frac{A_0}{R} e^{i\omega t} \left( kR \frac{J_0(kR)}{J_1(kR)} - 1 \right).
\]  

(4.17)

Two difficulties arise when we want to compare the peaks of the local strain defined by equation (4.17) with the resonances measured by the apparatus described in section 2.2.

1) The very existence of the solvent viscosity broadens the resonance peaks as soon as \( \omega > E/\eta \) so that it is difficult to determine their exact position, experimentally as well as theoretically.

2) As will be shown in the next paper, motion of the scattered light exists without any distortion of the latex: rigid motion of the sample also induces a change of the Kossel lines. This effect, which can be neglected for sharp resonances, cannot be ignored when the peaks begin to broaden.

One sees on figure 7 a typical curve showing the resonances of the quantity:

\[
|\psi(f)| = \frac{1}{R} \left| kR \frac{J_0(kR)}{J_1(kR)} - 1 \right|
\]  

(4.18)

plotted for a complex \( k \) and with \( R = 0.715, E = 40, \eta = 0.05 \) in CGS units. Since the resonances are
sharper for low frequencies a comparison between experiments and calculations has to be done in the low frequency part of the resonance spectrum. In this low frequency region the resonances appear for the zeros of the denominator \( J_1(kR) \) of equation (4.18), which can be calculated for positive real \( k \).

As quoted above, the smoothness of the peaks due to the imaginary part of \( k \) does not play an important role for low frequency. Let us define \( X_n \) as the \( n \)th zero of \( J_1(X) \) in the domain \( X > 0 \). Due to the definition of \( k \) (see Eq. (4.6)) the spectrum of the resonance frequencies simply writes:

\[
f_n = \left( \frac{E}{\rho} \right)^{1/2} \frac{1}{2\pi R} X_n. \tag{4.19}
\]

To a very good approximation, the difference between two consecutive zeros of \( J_1(X) \) can be considered as a constant, equal to \( \pi \). If we call \( \Delta f \) the difference between two consecutive resonance frequencies, we finally get

\[
E = \rho \frac{4}{R^2} (\Delta f)^2 \tag{4.20}
\]

which can be easily tested.

The difference between two peaks evaluated from equation (4.20) and for \( R = 0.715, E = 40 \) in CGS units is \( \Delta f = 4.42 \) Hz. This is a very good approximation of the exact value obtained from the plot of \( \psi(t) \) calculated for a complex \( k \). One obtains from figure 7 \( \Delta f = 4.48 \).

5. Measurements of the elastic modulus. — 5.1 Particle concentration dependence. — The regular shape of the vibrational spectra obtained with the sample B allowed to determine accurately the position of the resonance peaks and subsequently their average interval \( \Delta f \). Using the approximate formula (4.20) the elastic modulus \( E \) has been determined for the different particles concentrations (sample B) obtained by successive dilution as explained in section 3.1. The obtained variation \( E(n) \) is plotted in figure 8. One observes that the elastic modulus decreases with the concentration. For eightfold dilution the elastic modulus decreased by a factor of 65. For the concentration \( n = n_{\text{init}}/10 \) the suspension did not crystallize and we supposed that the elastic modulus vanishes.

In general, the elastic modulus can be determined from each spectrum with the accuracy

\[
\delta E/E = 2 \delta(\Delta f)/\Delta f
\]

which we estimated for the sample B to be in general of the order of 5%. However the dispersion of the experimental points in figure 9 is larger. We supposed that this can be due to the uncertainty in the ionic purity of the preparation — each dilution operation was followed by the ionic purification which was done without any control of the electric conductivity. For two preparations of the same particle concentration the ionic impurity concentration can be different and consequently the electrostatic interactions and the elastic modulus can be quite different.

5.2 Ionic impurities concentration dependence. — The fact, that the elastic modulus depends on the ionic impurities concentration, was verified in another series of measurements where the initial (sample B) preparation was doped with 0.001 N NaOH solutions in water. The base content in the sample was increased by steps; each step consisted in addition of four droplets of the electrolyte solution. The elastic modulus was measured and afterwards the relative electric conductivity was tested using two metallic electrodes immerged in the solution. As expected, the electric conductivity plotted on figure 9 as a function of the base content presents the V-like variation. The minimum conductivity corresponds to the neutralization of the acid groups and the negative charge of the polysterene spheres has been estimated to be \( 6 \times 10^3 \) e/part.

The elastic modulus of the colloidal crystal decreases as a function of the base content. For the base concen-
tration which corresponds to the minimum of the electrical conductivity the elastic modulus has been found to be finite (Fig. 10) and the crystal-liquid phase transition takes place for the base concentration larger than $c_{\text{min}}$. Such a behaviour seems to be in contradiction with the assumption of the acid groups neutralization for $c_{\text{min}}$ [12].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{elastic_modulus_variation}
\caption{Elastic modulus variation as a function of the Na$^+$ ion concentration.}
\end{figure}

5.3 Fine structure of the vibrational spectrum. — The spectra obtained with the sample A were in general much less regular than that of the sample B. The secondary resonance peaks, well visible in figure 4, were obtained systematically. An explanation of these secondary peaks can be proposed:

In a cylindrical sample vibrational modes other those that considered in section 4 can exist. In particular, due to the non slipping condition at the bottom of the test tube, the crystal deformation should also be a function of the vertical coordinate $Z$. In such a case two characteristic lengths must be taken into account: the tube radius $R$ and the sample length $H$.

The effect of the second length $H$ will be to introduce the fine structure in the spectrum because in general $H \gg R$. This fine structure can be visible only if the imaginary part of the elastic modulus (viscosity) is small enough, which seems to be the case for the sample B.

6. Conclusions. — From the preliminary results presented in this paper we can conclude that the spectrum of the mechanical vibrations excited and detected using the experimental set-up described in section 2, provides interesting information about the elastic modulus (complex in general) of the colloidal crystals. As compared with other methods, which we discussed in the introduction of this paper, our method is very simple and well adapted to measure accurately the low frequency elastic modulus in polycrystalline samples. In our samples, under specific conditions 1) of the particle size, charge and concentration and 2) of the ionic impurities concentrations, the elastic modulus has been found to vary between $10^2$ and $0 \text{ dyn/cm}^2$ which suggests that the differences between the results obtained previously [8, 9] can be explained in terms of the differences in the sample characteristics.

The present work can be extended in several directions:

I) A systematic measurement of the elastic modulus as a function of different parameters can be useful for the determination of the interaction potential in the colloidal crystals.

II) The application for the monocrystalline samples should be very interesting because in this case the measurement of the elasticity tensor is possible in principle and also because an additional information about the interaction potential could be obtained.

III) The vicinity of the crystal-liquid phase transition should be explored more in detail.

IV) The measurement of the imaginary part of the elastic modulus is of prime importance for the knowledge of the plastic properties of the colloidal crystals. Such a study should be made in connection with the microscopic observation of the dislocations mobility.

References

[12] Note added in proofs. The following explanation has been suggested to the authors: The crystal-liquid transition occurs due to the change in the potential which does not depend on the species of small ions. On the other hand, the neutralization is primarily the process of decreasing H$^+$ and increasing Na$^+$. Therefore, the minimum point of the conductivity does not have to coincide with the disappearance of the elastic modulus. This point should be mentioned.