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# Dynamics of colloidal crystals and colloidal liquids

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**Abstract.** The dynamics of strongly interacting colloidal particles is studied in the range of medium to high particle concentrations. Both the short-range ordered liquid phase and the long-range ordered crystal phase are investigated by means of photon correlation spectroscopy. The results are discussed in terms of a memory function formalism which is shown to be applicable for both the liquids and the crystals. The viscoelastic approximation for the memory function describes the experimental results in the liquid phase very well. For the first time results on single crystals are reported which exhibit a purely elastic behaviour. The theory enables us to extract information on the elastic moduli and sound velocities of the systems from the data, which in principle yield information on the particle interaction potential. The 'phonon' dispersion of colloidal crystals is also presented.

## 1. Introduction

Electrostatically stabilised colloids are nowadays widely used in chemical industries and have been the subject of scientific interest for a long period of time (e.g. Verwey and Overbeck 1948, Overbeck 1977). A most interesting problem in this field is the question of the interaction potential between colloidal particles which remains to be solved. A rather successful approach to tackle this problem is to study the dynamics of colloidal systems. These studies are also a basis for a better understanding of the interactions of linear polyelectrolytes and charged biological macromolecules, which play an important role in the living world. The invention of the photon correlation technique about ten years ago provided a very useful tool for these investigations, and since then a number of papers have appeared on the subject of the dynamics of interaction colloids or Brownian particles (e.g. Brown *et al* 1975, Schaefer 1977, Pusey 1978, Dalberg *et al* 1978, Grüner and Lehmann 1979, 1980a). Parallel to the progress in the experiments, the theoretical understanding was developed (e.g. Altenberger and Deutch 1973, Ackerson 1976, 1978, Hess and Klein 1978, 1979, 1980, 1981, Hess 1981). Although these theories are rather complex due to the statistical nature of the systems, the resemblance of these systems to simple liquids helps us to understand the physics involved. In some cases the colloids are even possible model systems to study features with light scattering techniques, which are very hard to observe in atomic systems, as for instance the long time tail of the velocity autocorrelation function (Pusey 1980). Another interesting feature of these suspensions is the fact that at high enough concentrations long-range order builds up and colloidal crystals are formed, which allow the observation of Bragg scattering by visible light (Hiltner and Krieger 1969, Williams and Crandall 1974, Schaefer and Ackerson 1975, Clark *et al* 1979). However, there are only a few experiments published, which deal

with the dynamical properties of these crystals (Dubois Violette *et al* 1980, Mitaku *et al* 1978), although their properties should render the interaction potential more easily accessible due to translational symmetry.

In this paper, firstly we will show that both the short-range ordered colloidal liquids and the long-range ordered colloidal crystals may be described by the same type of theory, namely a memory function formalism based on the Fokker–Planck equation. The memory function itself, which may be expressed in terms of wavevector dependent elastic moduli, is treated in a viscoelastic approximation for the ‘liquids’ and a purely elastic one for the ‘crystals’. The experimental data on the colloidal liquids confirm the assumption of viscoelastic behaviour and allow the determination of the memory function and its time dependence. The elastic moduli and the velocities of sound are extracted in the hydrodynamic limit. The first dynamical light scattering experiments from colloidal crystals, partly from large single crystals, are then presented. It was possible to extract the elastic modulus and a quasi-‘phonon’ dispersion. Since these data are closely related to the interaction potential between colloidal ‘atoms’, they yield information on the potential. It is shown that the usually screened Coulomb potential is not able to explain the data and some other form of the potential has to be assumed.

## 2. Theory

The dynamics of colloids may be derived from the Fokker–Planck equation. It has been shown by Hess (1980) that the more popular Smoluchowsky or Kirkwood equation leads to wrong answers in these strongly interacting systems. Therefore we start our discussion with an expression for the Laplace transform  $\tilde{F}(\mathbf{k}, \omega)$  of the intermediate scattering function obtained from the Fokker–Planck equation for a system of particle density  $\rho = N/V$  and mass  $m$  suspended in a viscous medium with friction coefficient  $\xi$

$$\tilde{F}(\mathbf{k}, \omega) = S(\mathbf{k}) \left( i\omega + \frac{k^2/[m\beta S(\mathbf{k})]}{i\omega + \xi/m + M_{\parallel}(\mathbf{k}, \omega)k^2/m\rho} \right)^{-1} \quad (1)$$

where  $\mathbf{k}$  is the wavevector and  $\beta = 1/k_B T$ . This expression is valid for moderate volume fraction of colloidal particles, where the electrostatic interaction dominates and therefore the hydrodynamic interaction may be neglected. The effects of the interaction between particles are described by the static structure factor  $S(\mathbf{k}) \equiv F(\mathbf{k}, t=0)$ , which is readily accessible experimentally, and the memory function  $\tilde{M}_{\parallel}(\mathbf{k}, \omega)$ , which is a  $\mathbf{k}$ - and  $\omega$ -dependent longitudinal viscosity (Hess 1981), describing the friction caused by interaction between the colloidal particles. Because of this physical meaning of the memory function  $M_{\parallel}$  we have chosen a different definition from that used by Dieterich and Peschel (1979). The expression of equation (1) is almost identical with that used in the theory of simple liquids (Hansen and McDonald 1976, p 320), except that in the case of colloids a separation of the viscosity of the solvent represented by  $\xi$  and an internal viscosity caused by particle–particle interactions represented by  $M_{\parallel}$  is introduced.

As indicated above, the memory function  $\tilde{M}_{\parallel}(\mathbf{k}, \omega)$  plays the essential role in the dynamics of strongly interacting systems. To deal with this complicated function we now make several simplifying assumptions. Firstly, we neglect the coupling of the

density fluctuations to the temperature fluctuations, which corresponds to  $c_p = c_v$  for the colloids. This should be a reasonable approximation for colloidal liquids and crystals since temperature fluctuations are mainly coupled to the solvent and decay very rapidly. We may then express  $M_{||}$  in terms of wavevector and frequency dependent transport coefficients:

$$\tilde{M}(\mathbf{k}, \omega) = \zeta(\mathbf{k}, \omega) + \frac{4}{3}\eta(\mathbf{k}, \omega). \tag{2}$$

In the hydrodynamic limit, these coefficients are the internal bulk ( $\zeta$ ) and shear ( $\eta$ ) viscosities. Secondly, we make the simplest approach for the time dependence of  $M_{||}$ , which is the viscoelastic approximation (Hansen and McDonald 1976, p 321)

$$M_{||}(\mathbf{k}, t) = [K_{\infty}(\mathbf{k}) + \frac{4}{3}G_{\infty}(\mathbf{k}) - \chi_s^{-1}(\mathbf{k})] \exp(-\Gamma_M(\mathbf{k})t) \tag{3}$$

where  $\Gamma_M$  is the relaxation constant of the longitudinal stress fluctuations. According to our first assumption, we do not have to distinguish between adiabatic ( $\chi_s$ ) and isothermal ( $\chi_T$ ) compressibility. Therefore we write

$$\chi(\mathbf{k}) = \chi_s(\mathbf{k}) = \chi_T(\mathbf{k}) = (\beta/\rho)S(\mathbf{k}). \tag{4}$$

The  $k$ -dependent transport coefficients introduced here are, in the limit  $\mathbf{k} \rightarrow 0$ , the instantaneous shear ( $G_{\infty}$ ) and bulk ( $K_{\infty}$ ) moduli (Zwanzig and Mountain 1965), whereas  $\chi(\mathbf{k} = 0)$  is the steady state compressibility of the system, that is  $\chi(\mathbf{k} = 0) = 1/K_0 \neq 1/K_{\infty}$ . Taking the Laplace transform of equation (3) and comparison with equation (2) yields

$$\tilde{M}_{||}(\mathbf{k}, \omega) = \zeta(\mathbf{k}, \omega) + \frac{4}{3}\eta(\mathbf{k}, \omega) = \frac{K_{\infty}(\mathbf{k}) + \frac{4}{3}G_{\infty}(\mathbf{k}) - \chi^{-1}(\mathbf{k})}{i\omega + \Gamma_M(\mathbf{k})}. \tag{5}$$

Combining this equation with our first equation, the starting point of our discussion, we now get an expression for the intermediate scattering function in terms of the generalised moduli introduced above:

$$\tilde{F}(\mathbf{k}, \omega) = S(\mathbf{k}) \left( i\omega + \frac{\omega_{i0}^2}{i\omega + \omega_s + \omega_{i2}^2/(i\omega + \Gamma_M(\mathbf{k}))} \right)^{-1}. \tag{6}$$

The following abbreviations have been introduced:

$$\begin{aligned} \omega_s &= \xi/m, & \omega_{i0}^2 &= \frac{k_B T}{mS(\mathbf{k})} k^2 = \frac{\chi^{-1}(\mathbf{k})}{m\rho} k^2, \\ \omega_{i1}^2 &= \frac{K_{\infty}(\mathbf{k}) + \frac{4}{3}G_{\infty}(\mathbf{k})}{m\rho} k^2, & \omega_{i2}^2 &= \omega_{i1}^2 - \omega_{i0}^2. \end{aligned}$$

The corresponding  $F(\mathbf{k}, t)$ , which is for instance determined by a light scattering experiment, is a sum of three exponentials

$$F(\mathbf{k}, t) = S(\mathbf{k})[\alpha_1 \exp(-\Gamma_1 t) + \alpha_2 \exp(-\Gamma_2 t) + \alpha_3 \exp(-\Gamma_3 t)].$$

However, two time regions may be distinguished. The first region corresponds to the time domain of fast variables with an approximate decay time and amplitude of

$$\Gamma_3 \approx \omega_s - \omega_{i1}^2/\omega_s, \quad \alpha_3 \approx \omega_{i0}^2/\omega_s^2. \tag{7}$$

For the colloidal systems under consideration,  $\omega_s$  is of the order of  $10^9 \text{ s}^{-1}$ , whereas  $\omega_i$  is several orders of magnitude smaller. Therefore we will neglect this component,

which does not show up in a Smoluchowsky approach, in our future considerations. We may do this since the amplitude is so extremely small and the time of decay is so short that we will never see any indication of that component in a photon correlation experiment.

The other two decay times are typical times of the colloidal systems and therefore much slower:

$$2\Gamma_{1,2} = \left( \Gamma_M + \frac{\omega_{i1}^2}{\omega_S} \right) \pm \left[ \left( \Gamma_M + \frac{\omega_{i1}^2}{\omega_S} \right)^2 - 4 \frac{\omega_{i0}^2 \Gamma_M}{\omega_S} \right]^{1/2},$$

$$2\alpha_{1,2} = 1 \pm \left( \frac{\omega_{i0}^2}{\omega_S} - \Gamma_M - \frac{\omega_{i2}^2}{\omega_S} \right) \left[ \left( \Gamma_M + \frac{\omega_{i1}^2}{\omega_S} \right)^2 - 4 \frac{\omega_{i0}^2 \Gamma_M}{\omega_S} \right]^{-1/2}. \quad (8)$$

The typical time scales may be examined by forming the first cumulant from  $\Gamma_1$  and  $\Gamma_2$ :

$$\Gamma_C = \alpha_1 \Gamma_1 + \alpha_2 \Gamma_2 = \frac{\omega_{i0}^2}{\omega_S} = \frac{D_0 k^2}{S(\mathbf{k})} = D_{\text{eff}} k^2. \quad (9)$$

This initial decay time lies well in the time range of photon correlation spectroscopy and has been verified both theoretically (Stephen 1971, Pusey 1975, Ackerson 1978) and experimentally (Brown *et al* 1975, Grüner and Lehmann 1979, 1980a) for colloids where hydrodynamic interactions are negligible. In writing equation (9) we have made contact with the more commonly used nomenclature in terms of effective or cooperative diffusion coefficients. We have written down the theory in terms of elastic moduli and not in diffusion coefficients purposely, since the language of elastic moduli intuitively suggests where the difference between liquids and solids has to be introduced.

However, the validity of the starting equation (1) is not at all obvious in the limit of a purely elastic crystal, since the equation is only an approximation by itself, because of the projection operator formalism used and the continuum approximation involved. But we will show that the formalism based on equation (1) in the elastic limit will describe the experiments very well.

The elastic limit is described by a purely imaginary viscosity and real elastic moduli. Hence we have to put  $\Gamma_M(\mathbf{k}) = 0$  in equation (3) and (5). We then obtain, apart from the 'fast' solution, equation (7), the following decay times and amplitudes:

$$2\Gamma_{1,2} = \frac{\omega_{i1}^2}{\omega_S} \pm \frac{\omega_{i1}^2}{\omega_S}, \quad 2\alpha_{1,2} = 1 \pm \frac{\omega_{i0}^2 - \omega_{i2}^2}{\omega_{i0}^2 + \omega_{i2}^2}. \quad (10)$$

Furthermore, the difference between instantaneous and steady state moduli is no longer relevant, which is a further simplification. We therefore may write in this approximation

$$\omega_{i0}^2 = \frac{K(\mathbf{k})}{m\rho} k^2, \quad \omega_{i1}^2 = \frac{K(\mathbf{k}) + \frac{4}{3}G(\mathbf{k})}{m\rho} k^2, \quad \omega_{i2}^2 = \frac{\frac{4}{3}G(\mathbf{k})}{m\rho} k^2.$$

It is seen that  $\omega_{i1}$  is the longitudinal acoustic phonon frequency, and by combining equations (10) and (11) we arrive at an intermediate scattering function which is a one exponential decay with a decay constant of

$$\Gamma_1 = \frac{\omega_{i1}^2}{\omega_S} = \frac{K(\mathbf{k}) + \frac{4}{3}G(\mathbf{k})}{\xi\rho} k^2. \quad (12)$$

This result was first derived by Tanaka *et al* (1973) for the quasielastic scattering

from gels, treating the gel as an elastic continuum. Therefore the result of equation (12) seems to be applicable to any elastic system overdamped by a viscous solvent, as long as the interaction between the elastic modes of the solvent and the system may be neglected (Marqusee and Deutch 1981), as it is always at low concentrations. The other component is a purely elastic scattering in the elastic limit. Its decay time goes to zero as

$$\Gamma_2 \approx (\omega_{i0}^2 / \omega_{i1}^2) \Gamma_M \quad (13)$$

as  $\Gamma_M$  goes to zero, whereas its amplitude does not vanish. We believe that this elastic scattering is only present at all  $k$  values due to the continuum approximation involved in equation (1) and that it will reduce to the Bragg scattering when translational symmetry is introduced.

With the result of equation (12), we have obtained a description of the experiment in terms of a well known friction ( $\omega_S$ ) and the longitudinal acoustic phonon frequency  $\omega_{i1}$ . For the latter, we may use the established theories of solid state physics to express the constants  $G(k)$  and  $K(k)$  in terms of the interaction potential. Unfortunately this is not an easy task and we will therefore have to restrict ourselves to a few remarks. Since the potential is spherically symmetric and the crystals are of cubic symmetry (Williams and Crandall 1974) we may describe the dynamics by means of two elastic constants,  $C_{11}$  and  $C_{44}$  ( $C_{12} = C_{44}$  according to Cauchy's relation). Furthermore, we may approximate these crystals with their rather long-range interactions to be isotropic. This approximation, which is reasonably fulfilled for NaCl, reduces the number of elastic constants further to one:

$$E = C_{11} = 3C_{44} = 3G = K + \frac{4}{3}G \quad (14)$$

where we have introduced a new modulus, the elastic modulus  $E$ . These considerations imply that at small wavevectors, that is where  $E = \text{constant}$ , we expect a simple  $k^2$  dependence of  $\Gamma_1$ , independent of the crystallographic direction. The modulus  $E$  is related to the second derivative of the interaction potential  $V(r)$  at the equilibrium positions of the particles (e.g. Born and Huang 1954):

$$E \approx \sum_i d_i^2 \rho \Delta V|_{d_i} \quad (15)$$

Here,  $d_i$  is the equilibrium distance between neighbouring atoms. A geometric factor, which depends on the exact crystallographic structure, is omitted, since in this paper we are going to discuss only qualitatively the  $\rho$  dependence of the interaction. In addition, it is quite clear that the summation in equation (15) has to be carried out for quite distant neighbours.

We will conclude the discussion of colloidal crystals by looking at the concentration dependence of the modulus  $E$  in equation (15) if we take the widely used screened Coulomb potential

$$V(r) = (Ze/\epsilon r) \exp[-\kappa(r-a)], \quad \kappa^2 = 4\pi\rho Ze^2/\epsilon k_B T,$$

which was also used for colloidal crystals (Joanny 1979). In the following, we will only look at proportionalities. Since  $\kappa \sim \rho^{1/2}$  and  $d_i \sim \rho^{-1/3}$  we end up with

$$E(\rho) = B\rho^{2/3} \exp(b'\rho^{1/2}) \exp(-b\rho^{1/6}) \quad (16)$$

where the constants of proportionality may be determined from the exact calculation.

From equation (16) the dependence of  $E$  on the concentration is seen to be rather complicated. In particular, the concentration enters as an exponent, which originates from the screening function  $\exp(-\kappa r)$ . This screening however, is characteristic also for more complicated potentials, which are derived from the linearised Poisson-Boltzmann equation like, for instance, those of Russel and Benzing (1981).

To summarise this section, we have shown that a memory function formalism based on the Fokker-Planck equation with a viscoelastic approach for the memory function, as is possibly the case in colloidal liquids, leads to a two-exponential decay of the intermediate scattering function. In a purely elastic approximation for the memory function, as should apply for colloidal crystals, a simple one-exponential decay is predicted, whose decay constant is given by the longitudinal sound frequency. This frequency may in principle be calculated from solid state theory. In the forthcoming sections, we will compare these predictions with our experimental data on colloidal liquids and colloidal crystals.

### 3. Experiments

The experiments were performed by photon correlation spectroscopy using light from either He-Ne laser ( $\lambda = 6328 \text{ \AA}$ ) or Argon laser ( $\lambda = 4579 \text{ \AA}$ ). The samples were contained in cylindrical quartz cells of 6 mm inner diameter immersed in a temperature stabilised bath of index matching fluid (glycerin). The scattered light was detected at different angles by either a RCA C31034 or an EMI 9862 photomultiplier and the intensity correlation functions formed by the minicomputer based 4000 channel quasi real time autocorrelator (Lehmann 1981). For a more detailed description of optical details see Grüner and Lehmann (1980a). All experiments were performed at a temperature of  $298 \pm 0.5 \text{ K}$ . The correlation functions were analysed using a multiexponential fit procedure developed by Provencher (1977). In all the experiments described here, it was necessary to correct for multiple scattering as described in Grüner and Lehmann (1980b) using the correlation functions of depolarised scattering. The field correlation function was calculated according to the Siegert relation

$$\langle I(\tau)I(0) \rangle = \langle I \rangle^2 (1 + A |g^{(1)}|^2)$$

assuming Gaussian statistics of the scattered light. This is justified by the fact that, according to the central limit theorem the scattering volume in both systems, the crystals and the liquids, may be subdivided in many subvolumes of identical properties.

The samples used were prepared from latex spheres of radius  $0.0455 \mu\text{m}$  and  $0.0425 \mu\text{m}$  supplied by DOW with a standard deviation of particle radius of 5%. The particles were suspended in carefully deionised water with a certain amount of mixed bed ion exchange resin (MB2, DOW-EX) permanently left in contact with the suspensions. From pH measurements we determined the surface charge of the spheres to be  $Q = 1000 \pm 150 e^-$  assuming that all protons emerge from the particles. When only the protons contribute to the screening of the electrostatic potential, the Debye screening length is calculated to be  $\kappa^{-1} = 2200 \text{ \AA}$  for the lowest and  $\kappa^{-1} = 310 \text{ \AA}$  for the highest concentration. This has to be compared with mean distance between particles of  $6000 \text{ \AA}$  and  $1900 \text{ \AA}$  respectively.

The concentrations given in this paper are determined from the dilution factor and the manufacturer's data on the concentration. Unfortunately there is some doubt

whether these concentrations are correct. The static light scattering measurements from colloidal crystals indicate a higher concentration by a factor of about 1.5. This is shown in table 1, where the crystal parameters for some of the colloidal crystals are calculated from the first Bragg peak assuming a BCC structure.

**Table 1.** The concentrations  $\rho_{\text{nom}}$  calculated from the dilution factor and the lattice constants  $d_{\text{BCC}}$  and experimental determined density  $\rho_{\text{BCC}}$  for different colloidal crystals assuming body centred cubic (BCC) crystal structure. The experimentally determined densities for a FCC crystal structure would be 8.9% larger.

$\rho_{\text{nom}}$ (cm <sup>-3</sup> )	$k_{\text{max}}$ (cm <sup>-1</sup> )	$d_{\text{BCC}}$ (cm)	$\rho_{\text{BCC}}$ (cm <sup>-3</sup> )	$\frac{\rho_{\text{BCC}}}{\rho_{\text{nom}}}$
$5.1 \times 10^{12}$	$1.39 \times 10^5$	$6.4 \times 10^{-5}$	$7.66 \times 10^{12}$	1.51
$10.1 \times 10^{12}$	$1.73 \times 10^5$	$5.13 \times 10^{-5}$	$1.48 \times 10^{13}$	1.47
$1.27 \times 10^{13}$	$1.90 \times 10^5$	$4.68 \times 10^{-5}$	$1.95 \times 10^{13}$	1.54
$1.6 \times 10^{13}$	$2.05 \times 10^5$	$4.33 \times 10^{-5}$	$2.46 \times 10^{13}$	1.53
$2.1 \times 10^{13}$	$2.25 \times 10^5$	$3.95 \times 10^{-5}$	$3.24 \times 10^{13}$	1.55
$2.6 \times 10^{13}$	$2.4 \times 10^5$	$3.70 \times 10^{-5}$	$3.94 \times 10^{13}$	1.52

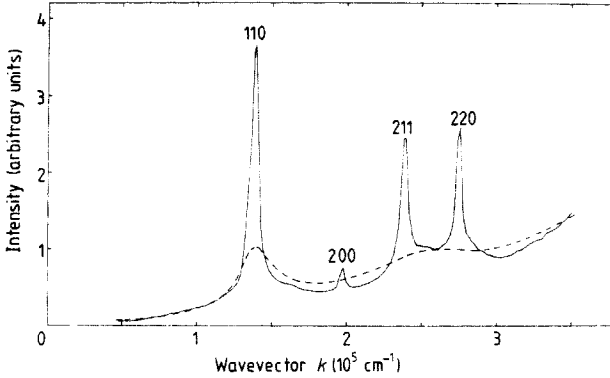
The ratio of the experimental density to the nominal density determined from the dilution factor is always 1.5 for the BCC structure, independent of particle size and different original solution supplied by DOW. There are only two possible explanations for this effect. The first would be a rather drastically inhomogeneous particle density. The crystal should be much more dense than the disordered colloid above the crystals. The second explanation, which we think is more likely, is a systematic error in the manufacturer's statement about the volume concentration.

In the concentration region of nominal  $2.5 \times 10^{12}$  particles/cm<sup>3</sup> up to approximately  $1.25 \times 10^{13}$  particles/cm<sup>3</sup> pronounced liquid-like order is obtained within several days from preparation. This order is very clearly seen in the static light scattering (Grüner and Lehmann 1979, 1980a). Depending on the preparation procedure and on the type of the ion exchange resin, samples left alone in the refrigerator for several months showed sharp Debye-Scherrer rings in a laser beam, indicating that polycrystalline samples had been formed. We have managed to obtain polycrystalline samples at nominal concentrations as low as  $5 \times 10^{12}$ . An example of the static light scattering for this concentration both as colloidal liquid and colloidal crystal is shown in figure 1. Apart from the relative intensities of the rings, the crystal pattern may be indexed according to a BCC lattice with the assignment of the rings shown in figure 1.

At even higher concentrations ( $\rho > 2.5 \times 10^{13}$  particles/cm<sup>3</sup>) large single crystals with a length of about 10 mm are obtainable. At concentrations below  $6 \times 10^{13}$  particles/cm<sup>3</sup> they exhibit a Laue-type scattering pattern. Above this concentration, the wavelength of the Argon laser is too long to fulfil the Bragg law. However, the formation of single crystals is very clearly seen from the extremely small turbidity of the single crystals.

It should be mentioned that mechanical disturbances like rocking tend to decrease the size of the crystals and crystallites. The effect of a mechanical shock is healed however within several hours and the crystals have remained stable over years up to now.





**Figure 1.** Static light scattering from a colloidal solution of latex spheres with diameter  $0.091 \mu\text{m}$  at nominal concentration of  $5 \times 10^{12}$  particles/cm<sup>3</sup> in the liquid (broken line) and crystalline (full line) phase. No corrections for multiple scattering and turbidity effects are made. The numbers are the indices of the Bragg peaks according to a BCC structure.

## 4. Results and discussion

### 4.1. Colloidal liquids

Most of the experimental data on the colloidal liquids has been published in earlier papers (Grüner and Lehmann 1979, 1980a). The purpose of this section is to review the data according to the theory in § 2 and to make a direct comparison with the data on colloidal crystals possible.

All measured intensity correlation functions were corrected for multiple scattering (Grüner and Lehmann 1980b), and it turned out that two exponentials were always sufficient to provide an excellent fit to the data. The two-exponential form of the functions is an experimental justification for the viscoelastic approximation made in § 2. The results for one particular concentration are shown in figure 2 together with the static structure factor  $S(k)$  from static light scattering measurements. It can be seen that the long-time decay constant goes towards the short-time decay for small  $k$  vectors.

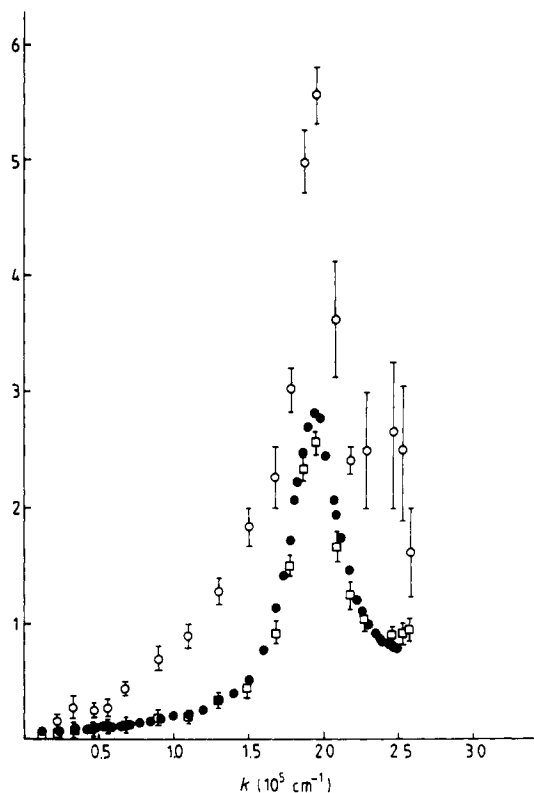
Since the samples are rather monodisperse, they do not show the incoherent self-diffusion term (Pusey 1980, Weisman 1980) present in previous experiments by Pusey (1978) and Dalberg *et al* (1978). From the data of the fit we are able to extract the memory function, which is, apart from numerical constants, the internal longitudinal viscosity. From equations (8), (6) and (5) it follows in the limit of  $\omega \rightarrow 0$  that

$$\tilde{M}_{\text{red}}(\mathbf{k}, \omega = 0) = \frac{k^2}{m\rho\omega_S} [\zeta(\mathbf{k}, \omega = 0) + \frac{4}{3}\eta(\mathbf{k}, \omega = 0)] = \frac{\Gamma_1 + \Gamma_2 - \Gamma_C - \Gamma_M}{\Gamma_M}. \quad (17)$$

$\Gamma_C$  is the first cumulant given by equation (9) and  $\Gamma_M$  is the decay constant of the memory function (equation (3)), which is given by the equation

$$\Gamma_M = \Gamma_1\Gamma_2/\Gamma_C. \quad (18)$$

With equation (17) we have defined a reduced, dimensionless quantity  $\tilde{M}_{\text{red}}$ . In our earlier papers (Grüner and Lehmann 1979, 1980a) we have analysed our data in terms of a memory function formalism based on the Smoluchowsky equation. The



**Figure 2.** Light scattering results from a colloidal liquid with nominal  $1.25 \times 10^{13}$  particles/cm<sup>3</sup>. Shown as a function of wavevector  $k$  are: ●  $S(k)$  the static structure factor; □  $(\Gamma_C/D_0k^2)^{-1}$  the reciprocal first cumulant  $\Gamma_C$  in units of  $D_0k^2$ ; ○  $(\Gamma_2/D_0k^2)^{-1}$  the reciprocal long-time decay constant in units of  $D_0k^2$ .

reduced memory function  $M'$  defined there is simply related to the Fokker-Planck based quantity  $\tilde{M}_{\text{red}}$  by (Hess 1981)

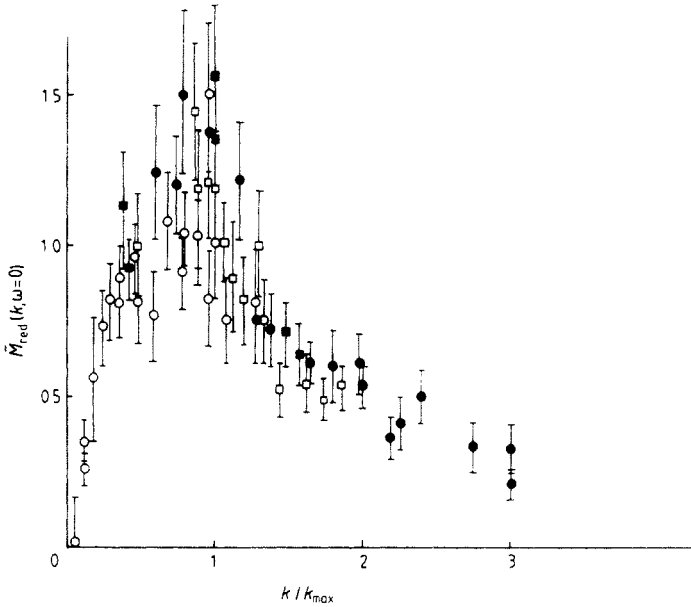
$$\tilde{M}_{\text{red}}(\mathbf{k}, \omega) = M'(\mathbf{k}, \omega) / (1 - M'(\mathbf{k}, \omega)). \quad (19)$$

This equation shows that the Smoluchowsky equation is only valid for  $M' \ll 1$ . In figure 3 the reduced memory function  $\tilde{M}_{\text{red}}(\mathbf{k}, \omega = 0)$  is plotted against a reduced wavevector  $k/k_{\text{max}}$ , where  $k_{\text{max}}$  is the position of the maximum of  $S(k)$ . Five different samples with different concentrations are included. They all seem to coincide on one universal function in this plot. It is seen that the friction due to the internal viscosity  $\zeta + \frac{4}{3}\eta$  (equation (17)) of the colloidal liquids is very strong and gets even larger than the friction of the solvent described by  $\xi = m\omega_S = 6\pi\eta_S\tilde{a}$ .

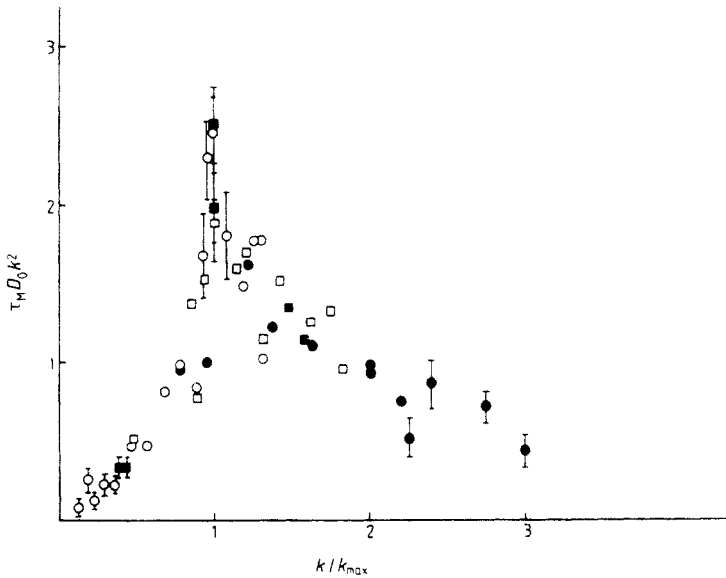
Within the viscoelastic approximation, which was shown to be valid experimentally, the memory function in the time domain (equation (3)) is a single exponential with the decay constant  $\Gamma_M$  given in equation (18). Defining a dimensionless quantity

$$\tau_{\text{red}} = D_0k^2/\Gamma_M, \quad (20)$$

we are able again to make a universal plot for all concentrations studied (figure 4). The dynamics of colloidal liquids is thus totally characterised by the static structure



**Figure 3.** The reduced memory function  $\tilde{M}_{red}(k, \omega = 0)$  for colloidal liquids. Different symbols apply to different nominal concentrations  $\rho$ :  $\bullet$   $2.5 \times 10^{12}$  particles/cm<sup>3</sup>;  $\square$   $5 \times 10^{12}$  particles/cm<sup>3</sup>;  $\blacksquare$   $7.5 \times 10^{12}$  or  $1.0 \times 10^{13}$  particles/cm<sup>3</sup>;  $\circ$   $1.25 \times 10^{13}$  particles/cm<sup>3</sup>.



**Figure 4.** The relaxation time  $\tau_M = \Gamma_M^{-1}$  of the viscoelastic memory function  $M_{ij}(k, t)$  in units of  $(D_0 k^2)^{-1}$ .

factor  $S(k)$  (compare figure 2) and a memory function described by the two parameters  $\tilde{M}_{red}(k, \omega = 0)$  and  $\tau_{red}$  in figures 3 and 4 respectively.

The last part of this section is devoted to a discussion of the hydrodynamic limit of  $\tilde{M}$  and  $\Gamma_M$ . It is seen from figure 3 that  $\tilde{M}_{red}$  goes to zero very fast for  $k = 0$ . This

is somehow unexpected since one would expect at least a  $k^2$  dependence in the vicinity of  $k = 0$ . It has been pointed out by Hess and Klein (1981) that a  $k^2$  dependence is only observable in a very small wavevector region ( $k/k_{\max} < 0.05$ ) which is extremely difficult to measure experimentally. Therefore all extrapolations towards  $k = 0$  have to be regarded with care. Nevertheless, we think that extrapolations provide useful information about the times and moduli involved characterising macroscopic properties of colloidal liquids. We have measured the low wavevector limit carefully in a sample with  $\rho = 1.25 \times 10^{13}$  particles/cm<sup>3</sup>, which has a high  $k_{\max}$  and therefore allows us to perform measurements down to  $k = 0.1 k_{\max}$ . In figure 5 the low wavevector results for  $\Gamma_M$  and for  $M_{\parallel}(k, t = 0)$  are shown where  $M_{\parallel}(k, t = 0)$  is given by

$$M_{\parallel}(k, t = 0) = (\Gamma_1 + \Gamma_2 - \Gamma_C - \Gamma_M) m \rho \omega_s / k^2.$$

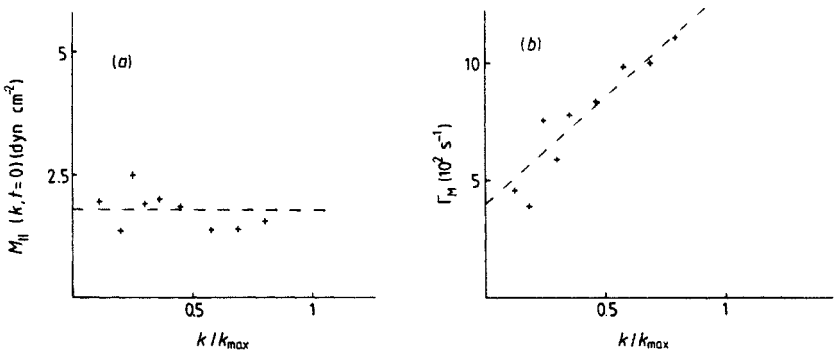


Figure 5. The low wavevector region of the memory function  $M_{\parallel}(k, t = 0)$  (a) and the relaxation constant  $\Gamma_M$  (b) for the sample with nominal  $1.25 \times 10^{13}$  particles/cm<sup>3</sup> (compare figure 2).

Whereas  $\Gamma_M$  decreases towards smaller wavevectors and extrapolates linearly to a value of about  $\Gamma_M(k = 0) = 4 \times 10^2 \text{ s}^{-1}$ ,  $M_{\parallel}(k, t = 0)$  stays almost constant at a value of  $1.9 \text{ dyn cm}^{-2}$ . According to equation (3),  $M_{\parallel}(k, t = 0)$  is the difference between the instantaneous moduli  $K_{\infty} + \frac{4}{3}G_{\infty}$  which are not hydrodynamic transport coefficients and the bulk modulus  $\chi^{-1}$ , which is a hydrodynamic coefficient in the low wavevector limit. Therefore, figure 5 provides a direct estimate of the instantaneous moduli, which are found to be about 30% larger than  $\chi^{-1}$  at  $k = 0$  (compare table 2). The sound velocity in the hydrodynamic region is (Hansen and MacDonald 1976, p 231)

$$c_i^2(k = 0) = k_B T / m S(k = 0). \tag{21}$$

It is interesting to compare this quantity with the results of the colloidal crystals and with usual liquids. Due to the very limited hydrodynamic region ( $k/k_{\max} < 0.05$ ) any extrapolation of measured data is dangerous. However, from the static structure factors (Grüner and Lehmann 1979, 1980a) it is possible to obtain values for  $S(k = 0)$  which should be correct within a factor of two. They are listed in table 2 together with the calculated compressibilities and sound velocities.

Although the above-mentioned uncertainties of the concentrations and of the extrapolation towards  $k = 0$  yield a systematic error of about  $-30\% + 40\%$  for  $c_i$  and of  $-50\% + 150\%$  for  $\chi^{-1}$ , the concentration dependence is unaffected and it is seen from table 2 and figure 8 that  $\chi^{-1} \sim \rho^2$  and  $c_i^2 \sim \rho$ , a behaviour which is different from the one of the colloidal crystals discussed in § 4.2.

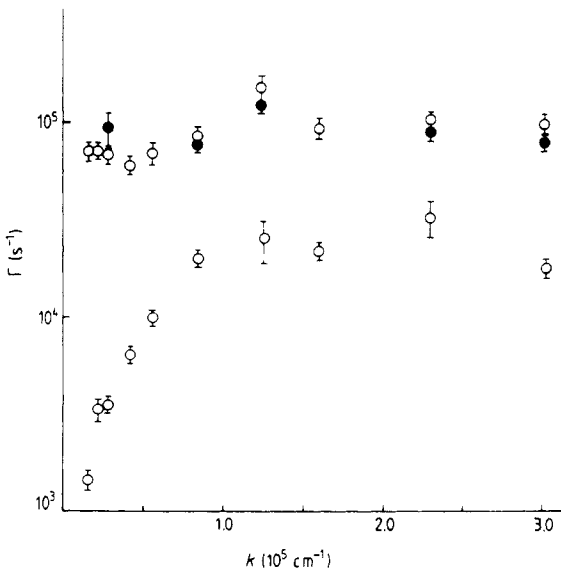
**Table 2.** The static structure factor  $S(k=0)$ , the bulk modulus  $\chi^{-1}$  and the longitudinal sound velocities of the colloidal crystals in the hydrodynamic limit. Accuracy is about a factor of two for  $S(k=0)$ . The densities are nominal densities (compare § 3).

$\rho$ ( $10^{12}$ particles/cm <sup>3</sup> )	$S(k=0)$	$\chi^{-1}$ (dyn cm <sup>-2</sup> )	$c_l$ (cm s <sup>-1</sup> )
2.5	0.30	0.29	17
5.0	0.23	0.78	20
7.5	0.14	2.0	26
10.0	0.11	3.3	29
12.5	0.07	6.3	35

#### 4.2. Colloidal crystals

Dynamical light scattering experiments on colloidal crystals seemed to be an unmanageable task due to the high concentrations of particle involved, since the tremendous multiple scattering obscured everything. When it became possible, however, to grow single crystals of centimeter size at moderate volume fractions of the order of one per cent, this problem was reduced by orders of magnitude. It is easily verified by comparing the turbidity of colloidal liquids or colloidal polycrystals with single crystals at the same concentration, that the latter are much more transparent and hence exhibit much less multiple scattering.

Looking at the experimental data for a single crystal (nominal concentration  $\rho = 6.2 \times 10^{13}$ ) in figure 6 it is seen that the polarised scattering is fitted by two exponentials, whereas the depolarised scattering is fitted by one exponential with a large decay constant  $\Gamma_{ms}$  which is not  $k$  dependent within experimental accuracy.



**Figure 6.** Dynamic light scattering results from a colloidal single crystal (particle diameter  $0.085 \mu\text{m}$  nominal concentration  $6.2 \times 10^{13}$  particles/cm<sup>3</sup>). The decay constants of the field correlation function are shown calculated from a fit to the intensity correlation function  $\circ$  VV scattering;  $\bullet$  VH scattering.

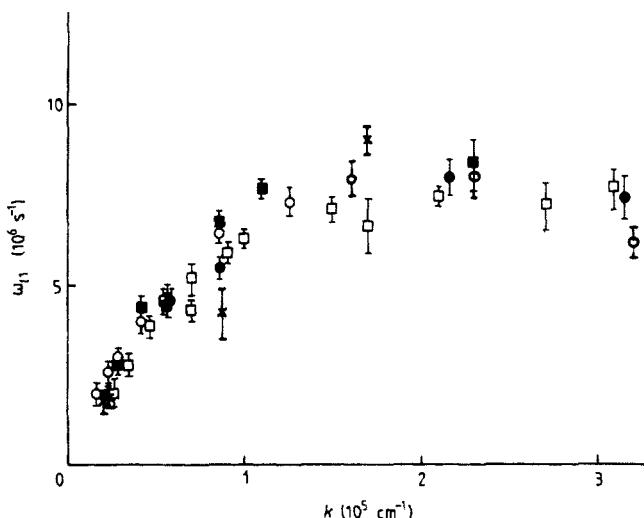
Moreover, measurements in HV-scattering geometry and, more important, in HH-scattering geometry, which is the polarised component of the multiple scattering at  $90^\circ$  scattering angle (compare Grüner and Lehmann 1980b), give also exponentials with the same decay constant  $\Gamma_{ms}$  within experimental accuracy. The same decay constant  $\Gamma_{ms}$  always occurs as the short time decay of the polarised scattering and we therefore attribute this wavevector independent short-time decay to multiple scattering.

Shear fluctuations, which should exhibit a wavevector dependence, are not observed in any depolarised scattering geometry.

The smaller decay constant in vv scattering is due to longitudinal fluctuations and there is only one single exponential decay observed. Comparison of the amplitude to background ratio  $\langle I^2 \rangle / \langle I \rangle^2$  for colloidal liquids and colloidal crystals, at concentrations where both states could be realised, shows almost identical values, except at the position of the Bragg peak. This is a hint that no elastic component is present between the Bragg peaks. Measurements to decay times of up to 10 ms gave no evidence for a slower decay, which would be present if the behaviour of the crystals were not purely elastic (equation (3)). The decay constants of the longitudinal modes are given by equation (10)

$$\Gamma = \omega_{l1}^2 / \omega_s$$

simply proportional to the square of the longitudinal phonon frequency. We are therefore able to extract the phonon dispersion for the colloidal crystals. This is shown in figure 7 for all crystals studied. Two different particle sizes ( $a = 0.042 \mu\text{m}$  and  $a = 0.045 \mu\text{m}$ ) and three different volume fractions (0.5%, 2% and 5% nominal) are shown. Surprisingly, all the different crystals show the same frequencies within



**Figure 7.** Phonon dispersion of colloidal crystals calculated from the experimental data according to equation (12). The different crystals are indicated by different symbols:  $\times$  nominal  $1.25 \times 10^{13}$  particles/cm<sup>3</sup> (particle diameter  $0.091 \mu\text{m}$ );  $\bullet$  nominal  $5.1 \times 10^{13}$  particles/cm<sup>3</sup> (particle diameter  $0.091 \mu\text{m}$ );  $\circ$  nominal  $6.2 \times 10^{13}$  particles/cm<sup>3</sup> (particle diameter  $0.085 \mu\text{m}$ );  $\square$  nominal  $12.5 \times 10^{14}$  particles/cm<sup>3</sup> (particle diameter  $0.091 \mu\text{m}$ );  $\blacksquare$  nominal  $1.55 \times 10^{14}$  particles/cm<sup>3</sup> (particle diameter  $0.085 \mu\text{m}$ ).

experimental accuracy. The small wavevector limit up to  $k \leq 0.5 \times 10^5 \text{ cm}^{-1}$  is conveniently described by a linear dispersion, leading to rather accurate values for the sound velocity

$$c_l = (E/m\rho)^{1/2}$$

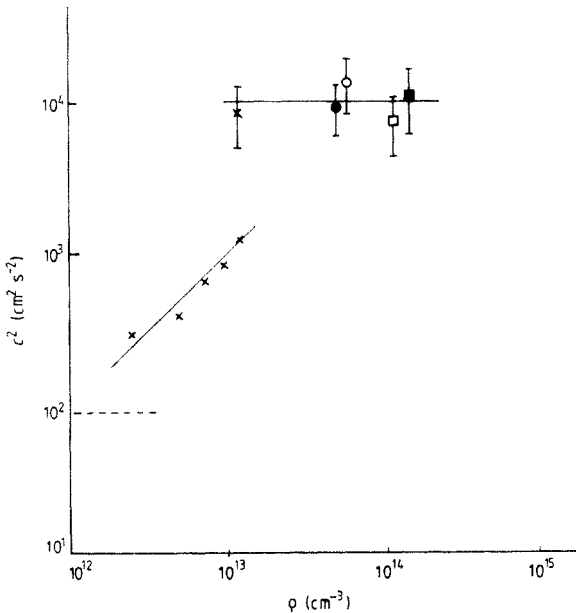
and for the elastic modulus  $E = K + \frac{4}{3}G$ .

From the fact that the crystals were not oriented with respect to the scattering plane, and hence the direction of  $\mathbf{k}$  varies from experiment to experiment, it may be concluded that the elastic behaviour is isotropic. Furthermore, comparison with table 1 shows that the  $\mathbf{k}$  region in figure 7 covers more than one Brillouin zone, and the dispersion is not a simple  $\sin(\mathbf{k}\mathbf{d})$  law, which would have been expected if only nearest-neighbour interactions played a role.

To analyse the dispersion further, the actual interaction potential has to be known, which unfortunately it is not, since the simple screened Coulomb potential does not apply, as we will show.

In figure 8 we compare the longitudinal sound velocities of the colloidal liquids and crystals. Whereas the colloidal liquids show sound velocities  $c_l^2 \sim \rho$ , the sound velocities of the crystals are constant ( $c_l = 100 \text{ cm s}^{-1}$ ) over the concentration regime measured. Moreover, there is a clear increase in sound velocity at the phase transition from liquid to solid at  $\rho = 1.25 \times 10^{13} \text{ particles/cm}^3$  of about a factor of 2.5.

The concentration independent sound velocity implies a linear dependence of the elastic moduli on the particle density which may be seen from the table 3 where the moduli and sound velocities are listed. The values for  $E$  may be compared with the results from shear experiments by Dubois Violette *et al* (1980), who obtain  $E = 110 \text{ dyn cm}^{-2}$  at particle density of  $2 \times 10^{13} \text{ cm}^{-3}$  and from ultrasonic measurements



**Figure 8.** Square of the sound velocities as a function of nominal particle concentration for colloidal liquids ( $\times$ ) and crystals (different symbols around  $10^4 \text{ cm}^2 \text{ s}^{-2}$ ). The broken line is the thermal sound velocity of a very dilute system  $c_{l0}^2 = k_B T/m$ .

**Table 3.** The elastic moduli and sound velocities of the colloidal crystals at small wavevectors. The densities are nominal densities (compare § 3). Crystals marked with + are prepared from particles with 0.085  $\mu\text{m}$  nominal diameter, the others from particles with diameter 0.091  $\mu\text{m}$ .

$\rho$ ( $10^{13}$ particles/cm <sup>3</sup> )	$E$ (dyn cm <sup>-2</sup> )	$c_l$ (cm s <sup>-1</sup> )
1.25	45	93
5.1	195	96
6.2+	255	116
12.5	420	86
15.5+	575	101

(Mitaku *et al* 1978) with  $G = 1200$  dyn cm<sup>-2</sup> at a density of  $3.6 \times 10^{13}$  particles/cm<sup>3</sup>. The latter value has been obtained at a frequency of  $7 \times 10^4$  s<sup>-1</sup>, which is not the low frequency limit as can be seen from figure 6.

The linear dependence of  $E$  on concentration, which was also observed by Dubois Violette *et al* (1980), cannot be explained by a screened Coulomb potential which should yield the concentration dependence of equation (16). Also, any other solution of the linearised Poisson-Boltzmann equation may be excluded, since any of these solutions (e.g. Hastings 1978, Russel and Benzing 1981) always leads to a strong nonlinear concentration dependence, in contradiction to our experiments and those of Dubois Violette *et al* (1980). We conclude that the elastic moduli and the phonon dispersion can give detailed information on the interaction potential of colloids. However, to extract this information, a detailed theoretical analysis is necessary, which is outside the scope of this paper.

## 5. Conclusions

In this paper we have given a summary of our experimental results on strongly interacting colloidal systems. The first dynamic light scattering experiments on colloidal single crystals were reported. Both the systems exhibiting long-range order, the colloidal crystals, and the systems showing short-range order, the colloidal liquids, are described by the same formalism. This memory function approach based on the Fokker-Planck equation, originally developed to describe the dynamics of simple liquids (Hansen and MacDonald 1976), turned out to be a perfect description for the colloidal crystals, if the viscoelastic approximation, which gives the features of the liquid, is converted to a purely elastic approximation.

With this theory, the experiments were discussed in terms of elastic moduli, which would give rise to phonons in condensed matter, whereas in colloids, these phonons are overdamped due to the friction of the solvent.

The main results of our investigation may be summarised as follows.

(1) For an appropriate discussion of strongly interacting colloids, the momenta of the colloidal particles have to be considered, or in other words, a description of colloidal liquids and colloidal crystals in terms of the Smoluchowsky equation fails.

(2) From the experiments, the velocities of sound may be extracted. There is a significant difference between the liquids and the crystals.

(3) The data from the colloidal crystals cannot be explained in terms of the widely used screened Coulomb or Debye-Hückel potential.



The last point clearly is not satisfactorily solved, since the question of the effective potential between charged particles is one of the central problems of colloidal science. We hope to get more quantitative information by solving the nonlinear Poisson-Boltzmann equation numerically and comparing the moduli and phonon dispersions thus obtained with the experimental data.

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### References

- Ackerson B J 1976 *J. Chem. Phys.* **64** 242  
 — 1978 *J. Chem. Phys.* **69** 684  
 Altenberger A R and Deutch J M 1973 *J. Chem. Phys.* **59** 894  
 Born M and Huang K 1954 *Dynamical Theory of Crystal Lattices* (Oxford: Oxford University Press)  
 Brown J C, Pusey P N, Goodwin J W and Ottewill R H 1975 *J. Phys. A: Math. Gen.* **8** 664  
 Clark N A, Hurd A J and Ackerson B J 1979 *Nature* **281** 57  
 Dalberg P S, Bøe A, Strand K A and Sikkeland T 1978 *J. Chem. Phys.* **69** 5473  
 Dieterich W and Peschel J 1974 *Physica* **95A** 208  
 Dubois Violette E, Pieranski P, Rothen F and Strzclecki L 1980 *J. Physique* **41** 369  
 Grüner F and Lehmann W 1979 *J. Phys. A: Math. Gen.* **12** L303  
 — 1980a in *Light Scattering in Liquids and Macromolecular Solutions* ed V Degiorgio, M Conti and M Giglio (New York: Plenum) p 51  
 — 1980b *J. Phys. A: Math. Gen.* **13** 2155  
 Hansen J P and McDonald J R 1976 *Theory of Simple Liquids* (London: Academic)  
 Hastings R 1978 *J. Chem. Phys.* **68** 675  
 Hess W 1980 in *Light Scattering in Liquids and Macromolecular Solutions* ed V Degiorgio, M Conti and M Giglio (Plenum: New York) p 31  
 — 1981 *J. Phys. A: Math. Gen.* **14** L 145  
 Hess W and Klein R 1978 *Physica* **94A** 71  
 — 1979 *Physica* **99A** 463  
 — 1980 *J. Phys. A: Math. Gen.* **13** L5  
 — 1981 *Physica* **105A** 552  
 Hiltner P A and Krieger I M 1969 *J. Phys. Chem.* **73** 2386  
 Joanny J F 1979 *J. Coll. Interf. Sci.* **71** 622  
 Lehmann W P 1981 *J. Phys. E: Sci. Instrum.* **14** 709  
 Marqusee J A and Deutch J M 1981 *J. Chem. Phys.* **75** 5239  
 Mitaku S, Ohtsuki T, Enari K, Kishimoto A and Okano K 1978 *Japan. J. Appl. Phys.* **17** 305  
 Overbeck J Th G 1977 *J. Coll. Interf. Sci.* **58** 408  
 Paul G L and Pusey P N 1981 *J. Phys. A: Math. Gen.* **14** 3301  
 Provencher S W 1976 *J. Chem. Phys.* **64** 2772  
 Pusey P N 1975 *J. Phys. A: Math. Gen.* **8** 1433  
 — 1978 *J. Phys. A: Math. Gen.* **11** 119  
 — 1980 in *Light Scattering in Liquids and Macromolecular Solutions* ed V Degiorgio, M Conti and M Giglio (New York: Plenum) p 1

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- Russel W B and Benzing D W 1981 *J. Coll. Interf. Sci.* **83** 163, 178  
Schaefer D W 1977 *J. Chem. Phys.* **66** 3980  
Schaefer D W and Ackerson B J 1975 *Phys. Rev. Lett.* **35** 1448  
Stephen M J 1971 *J. Chem. Phys.* **55** 3878  
Tanaka T, Hocker L O and Benedek G B 1973 *J. Chem. Phys.* **59** 5151  
Verwey E J and Overbeck J Th G 1948 *Theory of the Stability of Lyophobic Colloids* (New York: Elsevier)  
Weisman M B 1980 *J. Chem. Phys.* **72** 231  
Williams R and Crandall R S 1974 *Phys. Lett.* **48A** 225  
Zwanzig R and Mountain R D 1965 *J. Chem. Phys.* **43** 4464