

LIGHT SCATTERING FROM A BINARY MIXTURE  
OF LATEX SPHERES

By

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OF LATEX SPHERES

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION. . . . .	1
II. THEORY. . . . .	3
III. EXPERIMENTAL APPARATUS AND PROCEDURE. . . . .	14
IV. RESULTS . . . . .	18
Undoped Sample . . . . .	18
Doped Sample . . . . .	23
V. DISCUSSION. . . . .	28
BIBLIOGRAPHY. . . . .	33
APPENDIX - DERIVATION OF EQUATIONS 2.8 AND 2.9. . . . .	34

## LIST OF FIGURES

Figure	Page
1. Definition of Scattering Vector. . . . .	4
2. Pair Distribution Function for a Typical Liquid. . . . .	8
3. Structure Factor for a Typical Liquid. . . . .	9
4. Diagram for DLS and SLS Apparatus. . . . .	16
5. Structure Factor for the Undoped Sample. . . . .	19
6. $q^2/K_1$ Versus $q$ for the Undoped Sample. . . . .	21
7. $\ln(C(q,t))$ Versus $q^2t$ for Doped Sample at $40^\circ$ . . . . .	22
8. $q^2/K_L$ Versus $q$ for the Undoped Sample. . . . .	24
9. Structure Factor for the Doped Sample. . . . .	25
10. $q^2/K_1$ Versus $q$ for the Doped Sample. . . . .	26
11. $q^2/K_L$ Versus $q$ for the Doped Sample. . . . .	27
12. Plot of Estimated $S_{12}$ . . . . .	30

## CHAPTER I

### INTRODUCTION

With the advent of the laser two major hinderances to light scattering are overcome: low intensity levels and lack of monochromaticity. While there are many kinds of light scattering we shall only consider two in this thesis: static light scattering (SLS) and dynamic light scattering (DLS) or light beating spectroscopy.

Static light scattering is a technique which involves measuring intensity as a function of scattering angle. It gives us a tool for investigating structures on the order of several thousand angstroms (since the wavelengths used are around 5500 angstroms), just as X-ray scattering is used to probe interatomic structures in fluids and solids.

Dynamic light scattering monitors the fluctuations in the intensity as a function of scattering angle. This technique, which utilizes a digital correlator or spectrum analyzer linked to a photomultiplier tube (PMT), produces data in the form of a photon correlation function  $C(q,t)$ . Here  $\underline{q}$  is the scattered wave vector and  $t$  is the correlation delay time. This correlation function when measured for colloidal suspensions may be related to the dynamics of the particles in suspension, much as the correlation function or spectrum measured for pure fluids and solids by inelastic neutron scattering may be related to the dynamics of atomic motions.

Theoretically the initial dynamics of the particle motion (measured

by DLS) may be related to the static structure (measured by SLS). This relationship for colloids has been confirmed extensively by combined DLS and SLS measurements from dilute but highly charged monodisperse spherical microparticle suspensions. In this work we extend these combined DLS and SLS measurements to a binary mixture of dilute but highly charged spherical microparticles. We have indication of an unusual structure observed by SLS while DLS measurements produce results which are only partially consistent with a generalized initial decay theory for the correlation function. These results are important for two reasons: (1) because they challenge our present understanding of light scattering from colloids, and (2) because they put in question recent measurements of self-diffusion.

Before the experimental results are presented and a discussion is given, we present the standard theory for SLS and DLS which is to be applied to the systems under study.



## CHAPTER II

### THEORY

We first consider scattering from large particles in a suspension in the Born approximation. An incident plane wave with wave vector  $\underline{k}_i$  induces a time varying dipole moment in the scattering particle. If it is assumed that the scatterer is only weakly coupled electrically to the other surrounding particles, then the total re-radiated or scattered electric field due to the oscillating dipoles can be expressed as a sum of the amplitudes due to each particle,  $i$ , in the illuminated volume (neglecting multiple scattering), e.g. (1).

$$E_S(\underline{q}, t) = \sum_i b_i(\underline{q}) \exp(i\underline{q} \cdot \underline{r}_i(t)) \quad (2.1)$$

Here  $\underline{r}_i$  is the  $i^{\text{th}}$  particle position and  $\underline{q}$  is the scattering wave vector which is defined as

$$\underline{q} = \underline{k}_i - \underline{k}_S$$

with  $\underline{k}_S$  being the wave vector scattered in the direction of observation (see Figure 1), e.g. (2). Assuming the scattering to be quasi-elastic,  $|\underline{k}_i| = |\underline{k}_S|$ , gives the magnitude of  $\underline{q}$  as

$$q = 4\pi n \sin(\theta/2)/\lambda$$

where  $n$  is the index of refraction of the medium,  $\theta$  is the scattering angle, and  $\lambda$  is the incident wavelength, e.g. (3).

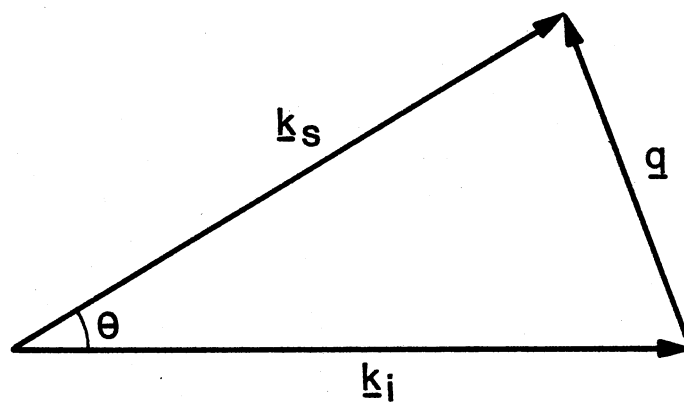


Figure 1. Definition of Scattering Vector

The average intensity of the scattered radiation, which is measured in SLS, is defined as

$$I(\underline{q}) = \langle |E_S(\underline{q}, t)|^2 \rangle$$

If there are a large number of identical particles,  $N$ , (a monodisperse suspension) where  $b_i = b_j = b$  for all  $i$  and  $j$ , then using Equation 2.1 the average scattered intensity becomes

$$\langle I(\underline{q}) \rangle = Nb^2(\underline{q})S(\underline{q})$$

where  $S(\underline{q})$  is the static structure factor which is given by

$$S(\underline{q}) = (1/N) \sum_{i=1}^N \sum_{j=1}^N \langle \exp(i\underline{q} \cdot (\underline{r}_i - \underline{r}_j)) \rangle \quad (2.2)$$

For small spherical particles, as studied in our experiments, the  $b$ 's are essentially independent of  $\underline{q}$  and the average scattered intensity is simply proportional to  $S(\underline{q})$ .

We define a particle number density as

$$\rho(\underline{r}) = \sum_{i=1}^N \delta(\underline{r} - \underline{r}_i)$$

where  $\langle \rho \rangle = N/V$  for  $N$  particles in a volume  $V$ . The Fourier transform of this is

$$\begin{aligned} \hat{\rho}(\underline{q}) &= \int \exp(-i\underline{q} \cdot \underline{r}) \rho(\underline{r}) d\underline{r} \\ &= \sum_{i=1}^N \exp(-i\underline{q} \cdot \underline{r}_i) \end{aligned}$$

which gives us a means of expressing the structure factor (mean intensity) in terms of number density fluctuations. For example, from Equ-

tion 2.2:

$$S(\underline{q}) = (1/N) \langle \hat{\rho}(\underline{q}) \hat{\rho}(-\underline{q}) \rangle$$

The structure factor can also be developed from a two particle distribution function,

$$g(\underline{r}_1, \underline{r}_2) = V^2 \langle \delta(\underline{r}_1 - \underline{r}_1') \delta(\underline{r}_2 - \underline{r}_2') \rangle,$$

which is the probability of finding a particle at  $\underline{r}_1$  if there is a particle at  $\underline{r}_2$ . Using this and working from Equation 2.2 we find

$$\begin{aligned} S(\underline{q}) &= (1/N) \sum_i^N \sum_j^N \langle \exp(-i\underline{q} \cdot \underline{r}_i) \exp(i\underline{q} \cdot \underline{r}_j) \rangle \\ &= 1 + (1/N) \sum_i \sum_j \langle \iint \exp(-i\underline{q} \cdot (\underline{r}_1 - \underline{r}_2)) \delta(\underline{r}_1 - \underline{r}_i) \delta(\underline{r}_2 - \underline{r}_j) d\underline{r}_1 d\underline{r}_2 \rangle \end{aligned}$$

If the choice of origin is arbitrary (translational invariance), then  $g(\underline{r}_1, \underline{r}_2) = g(\underline{r}_1 - \underline{r}_2) = g(\underline{r})$ ,

$$\begin{aligned} S(\underline{q}) &= 1 + (N(N-1)/NV^2) \iint \exp(-i\underline{q} \cdot (\underline{r}_1 - \underline{r}_2)) g(\underline{r}_1 - \underline{r}_2) d\underline{r}_1 d\underline{r}_2 \\ &= 1 + \langle \rho \rangle \int \exp(-i\underline{q} \cdot \underline{r}) g(\underline{r}) d\underline{r} \end{aligned}$$

and can be written as a pair correlation function by

$$h(\underline{r}) = g(\underline{r}) - 1$$

and the structure factor becomes

$$\begin{aligned} S(\underline{q}) &= 1 + \langle \rho \rangle \int \exp(-i\underline{q} \cdot \underline{r}) h(\underline{r}) d\underline{r} + (2\pi)^3 \langle \rho \rangle \delta(\underline{q}) \\ &= 1 + \langle \rho \rangle \hat{h}(\underline{q}) \end{aligned}$$

where  $\hat{h}(\underline{q})$  is the Fourier transform of the pair correlation function and the delta function can be ignored since it corresponds to forward scattering.

Figure 2 shows the radial distribution function,  $g(\underline{r})$ , for a typical liquid. The principal peak occurs at the nearest neighbor distance,  $r_0$ , and the subsequent peaks are of decreasing amplitude indicating that the more distant neighbors are less correlated with a particle at the origin, with  $g(r) \rightarrow 1$  (completely uncorrelated;  $h(r) \rightarrow 0$ ) as  $r \rightarrow \infty$ . These same features are displayed by the structure factor which is seen in Figure 3, although they have a different interpretation.

Since our study deals with a binary system, we need to generalize for two species,  $b_1$  and  $b_2$ . The structure factor is related to the mean intensity by

$$\langle I(\underline{q}) \rangle = (n_1 b_1^2 + n_2 b_2^2) S(\underline{q})$$

where  $n_1$  and  $n_2$  are the numbers of each species. The structure factor now has three terms.

$$S(\underline{q}) = (1/(n_1 b_1^2 + n_2 b_2^2)) (S_{11} + S_{22} + S_{12}) \quad (2.3)$$

where

$$S_{11} = b_1^2 \sum_i^{N_1} \sum_j^{N_2} \exp(i\underline{q} \cdot (\underline{r}_{1i} - \underline{r}_{1j}))$$

$$S_{22} = b_2^2 \sum_i^{N_1} \sum_j^{N_2} \exp(i\underline{q} \cdot (\underline{r}_{2i} - \underline{r}_{2j}))$$

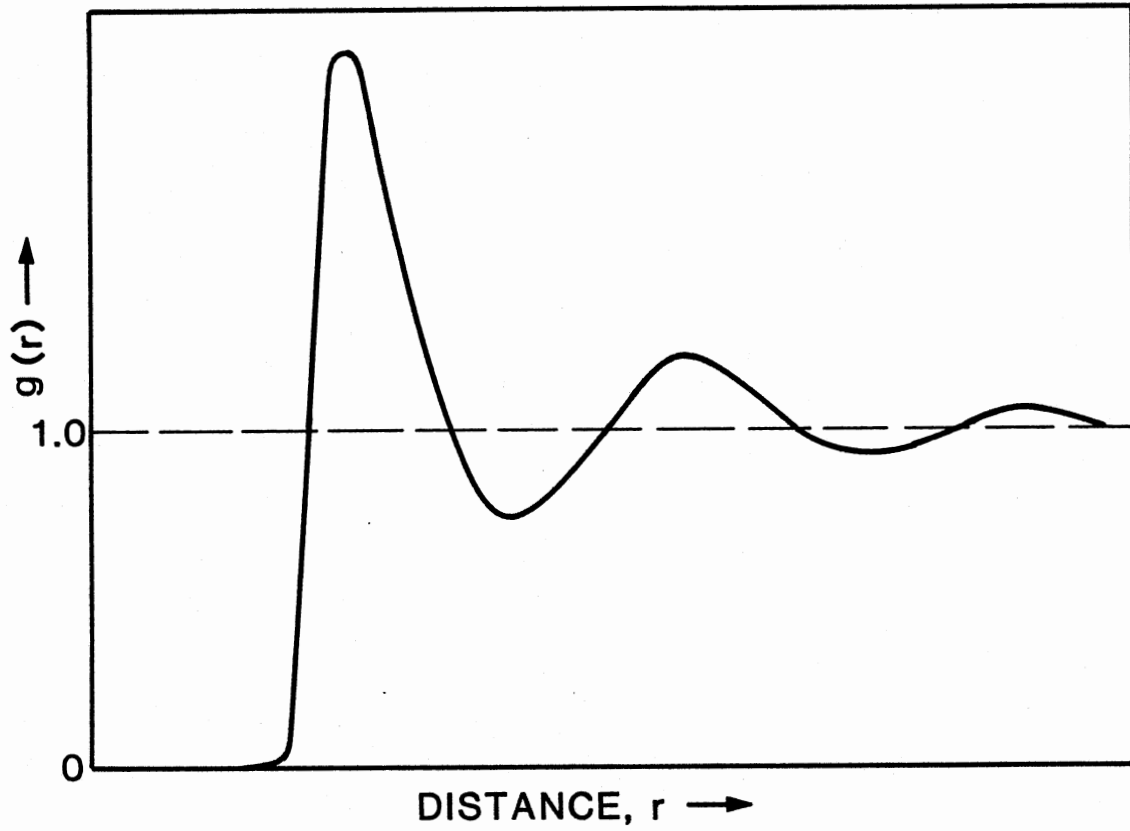


Figure 2. Pair Distribution Function for a Typical Liquid

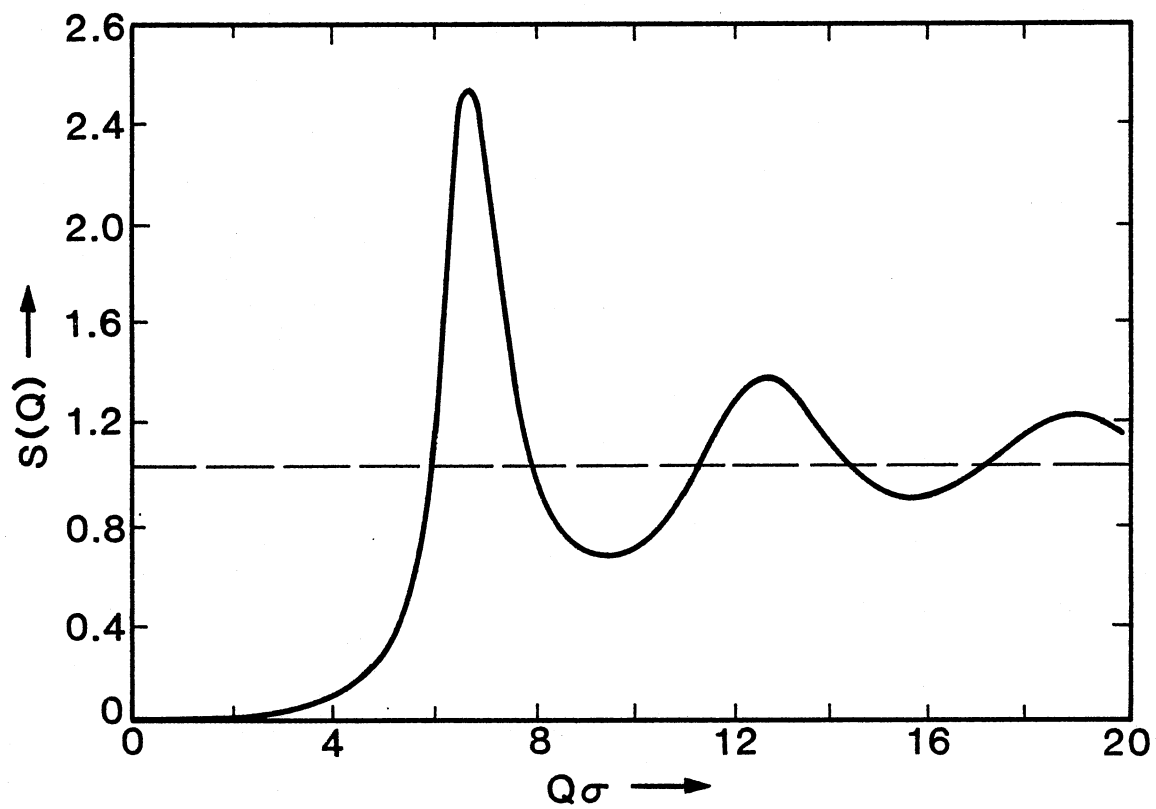


Figure 3. Structure Factor for a Typical Liquid

$$\begin{aligned}
 S_{12} &= b_1 b_2 \left( \sum_i^1 \sum_j^2 \exp(i\mathbf{q} \cdot (\mathbf{r}_{1i} - \mathbf{r}_{2j})) + \sum_i^1 \sum_j^2 \exp(-i\mathbf{q} \cdot (\mathbf{r}_{1i} - \mathbf{r}_{2j})) \right) \\
 &= 2b_1 b_2 \sum_i^1 \sum_j^2 \cos(\mathbf{q} \cdot (\mathbf{r}_{1i} - \mathbf{r}_{2j}))
 \end{aligned}$$

One term corresponds to correlations between any two large particles,  $S_{11}$ , and another to correlations between any two small particles,  $S_{22}$ . The third term,  $S_{12}$ , involves correlations between the two species; large to small and small to large.

In DLS the measured photon count correlation function can be expressed as an intensity correlation function, and for a large number of independent correlation regions in the scattering volume (gaussian approximation), this function has a simple representation in terms of the electric field correlations,  $g^{(1)}(\mathbf{q}, t)$ , and consequently particle correlations. Here we have

$$\begin{aligned}
 C(\mathbf{q}, t) &= \langle I(\mathbf{q}, t) I(\mathbf{q}, 0) \rangle \\
 &= B(1 + c/g^{(1)}(\mathbf{q}, t)/^2)
 \end{aligned}$$

where

$$g^{(1)}(\mathbf{q}, t) = \langle E_S(\mathbf{q}, t) E_S^*(\mathbf{q}, 0) \rangle / \langle E_S / ^2 \rangle,$$

$B$  is the background (baseline), and  $c$  is an apparatus constant which is determined by such things as detector distance and other geometric factors.

In correspondence with the argument given for SLS, we define a particle correlation or probability distribution as



$$\begin{aligned}
 P(\underline{r}, t) &= (1/N) \langle \rho(\underline{r}(t)) \rho(\underline{r}(0)) \rangle \\
 &= (1/N) \sum_i^N \sum_j^N \langle \delta(\underline{r}_i(t)) \delta(\underline{r}_j(0)) \rangle
 \end{aligned}$$

The Fourier transform of this gives what is called the intermediate scattering function,  $F(\underline{q}, t)$ .

$$\begin{aligned}
 \hat{P}(\underline{q}, t) = F(\underline{q}, t) &= (1/N) \langle \hat{\rho}(\underline{q}(t)) \hat{\rho}(\underline{q}(0)) \rangle \\
 &= (1/N) \sum_i^N \sum_j^N \langle \exp(-i\underline{q} \cdot (\underline{r}_i(t) - \underline{r}_j(0))) \rangle
 \end{aligned}$$

By observing that  $F(\underline{q}, t)$  evaluated at  $t = 0$  is equal to  $S(\underline{q})$ , we have a means of re-expressing the correlation function for the scattered electric field amplitude by simply normalizing the intermediate scattering function.

$$\begin{aligned}
 g^{(1)}(\underline{q}, t) &= F(\underline{q}, t) / F(\underline{q}, 0) \\
 &= F(\underline{q}, t) / S(\underline{q})
 \end{aligned}$$

In order to gain a better understanding of the nature of the measured correlation function we consider the special case of independent particles undergoing random (self) diffusion. The probability of a particle starting at the origin and diffusing to the point  $\underline{r}$  in the time  $t$  by a random walk is governed by the diffusion equation

$$\frac{\partial}{\partial t} P(\underline{r}, t) = D_0 \nabla^2 P(\underline{r}, t) \quad (2.4)$$

where  $D_0$  is the self-diffusion coefficient. The spacial Fourier transform of 2.4 yields

$$\frac{\partial}{\partial t} \hat{P}(\underline{q}, t) = -q^2 D_0 \hat{P}(\underline{q}, t) \quad (2.5)$$

where

$$\begin{aligned} \hat{P}(\underline{q}, t) &= \int \exp(i\underline{q} \cdot \underline{r}) P(\underline{r}, t) d\underline{r} \\ &= (1/N) \sum_i^N \langle \exp(i\underline{q} \cdot (\underline{r}_i(t) - \underline{r}_i(0))) \rangle \end{aligned}$$

This is simply the intermediate scattering function where all the cross-terms (interactions) are trivially zero and is normally called the self-intermediate scattering function,  $F_S(\underline{q}, t)$ . By setting  $t = 0$ , we find  $S(\underline{q}) = 1$  for all  $\underline{q}$  which indicates no angular dependence in the scattered intensity or no spacial correlations when there are no interactions.

The differential Equation 2.5 has the solution

$$\hat{P}(\underline{q}, t) = F_S(\underline{q}, t) = \exp(-q^2 D_0 t)$$

which gives a correlation function which is a single exponential

$$C(q, t) = B(1 + c \exp(-2q^2 D_0 t))$$

Though this result is convenient and is used extensively for determining  $D_0$  for dilute independent particle systems, it must be extended for this study since the samples used are highly interacting and highly correlated. Because the interactions make the systems more difficult to analyze theoretically and experimentally, several procedures have been developed for the analysis.

One method used to examine the correlation function for interacting

systems is called the cumulant expansion, where  $g^{(1)}(q,t)$  is fit to a function of the form

$$g^{(1)}(q,t) = \exp(-K_1 t + K_2 t^2/2! + \dots) \quad (2.6)$$

for as many  $K_i$ , cumulants, as necessary. Two cumulants is usually sufficient to arrive at a good fit to the data. For a non-interacting system,  $K_1$  is expected to be  $D_0 q^2$  (constant) and all other cumulants zero. So, in a two cumulant fit the second cumulant is a measure of the variation of the correlation function from a single exponential.

The diffusion equation may be generalized for the case where the particles are under the influence of mutual forces,  $f_{ij}$ , with the result

$$\frac{\partial}{\partial t} P = D_0 \sum_i^N (\nabla_i^2 + \beta \nabla_i f_{ij}) P \quad (2.7)$$

When this equation is solved and expressed in terms of the expansion 2.6, the first cumulant is found to be

$$K_1 = D_0 q^2 / S(q) \quad (\text{See Appendix}) \quad (2.8)$$

which relates the initial slope of the natural log of the correlation function,  $K_1$ , to what can be measured in the statics,  $S(q)$ . Again we must generalize this result to a two species system with the result

$$K_1 = (n_1 b_1^2 D_1 + n_2 b_2^2 D_2) q^2 / S(q) N \quad (2.9)$$

where  $D_1$  and  $D_2$  are the self-diffusion rates for each species multiplied in each case by the scattering fraction for that species.

## CHAPTER III

### EXPERIMENTAL APPARATUS AND PROCEDURE

There are two samples under study in this work. Both samples consist of Dow polystyrene spheres suspended in deionized water with a small amount of mixed-bed ion exchange resin (Dowex) to remove all salt ions to allow the highly charged latex spheres to interact.

One sample, called the undoped sample, was simply a suspension of .038 micron diameter beads at a concentration of  $3.0 \times 10^{12}$  particles/ml. This sample is to act as a control by firstly showing the type of structure to be expected with an interacting system and secondly to show that any structure present in the mixture, the doped sample, is not due to the smaller, .038, background particles. This concentration gives a mean particle separation of .69 microns.

The second, doped, sample is a mixture of two sphere sizes. To the background concentration of .038 micron spheres is added some larger, .109 micron, spheres at a concentration of  $3.0 \times 10^{10}$  particles/ml or about one hundredth the background concentration which gives a total concentration of all spheres of  $3.03 \times 10^{12}$  particles/ml. The sample was chosen originally so that we have a low concentration of strong scatterers imbedded in a sea of smaller spheres which are expected to contribute less to the total scattered intensity. At the concentration of the larger spheres alone we expect a mean particle separation of 3.2 microns. The relative scattering of large to small is estimated to be

around 10.

The samples were prepared and placed in holders in February of 1981. The sample holders are quartz cuvettes, .1 cm x 1 cm x 3.5 cm, capped with teflon and sealed with clay to avoid contamination.

The apparatus (see Figure 4) for DLS and SLS is the same. In SLS the total photon count is read from the correlator for 20 second runs. The laser, Spectra Physics 5 mW Model 120 He-Ne (6328 angstrom), and lens are mounted on one optical bench and the pinhole, stop, and photomultiplier tube (PMT) on another with the two benches connected by a pivot and the sample sitting at the pivot point. The PMT can then be swept through all scattering angles from  $0^{\circ}$  to  $125^{\circ}$ . The PMT with discriminator, amplifier, and power supply is made by Pacific Photometric Instruments, and the 4-bit, 64 channel digital correlator is from Langley-Ford Instruments which was used in the unclipped mode. The sample times for various runs were chosen to give a complete picture of the correlation function, and the run time was such that there was a total count of  $10^6$  counts or greater (channel noise  $\sigma N/N$  around .1%). The signal to noise was generally less than or approximately .6. The correlation function was visually monitored during the data runs on a Tectronics T922 oscilloscope. All 80 channels of each run are then stored in data files on floppy disk by a PDP-11 mini-computer. This computer and a LSI-11 mini-computer were also used for the data analysis.

The majority of the data was taken over a one week period in August of 1981. These runs were also compared to data taken earlier during March and June of the same year to note structural time dependence or deterioration of the samples (see results and discussion). Water bath

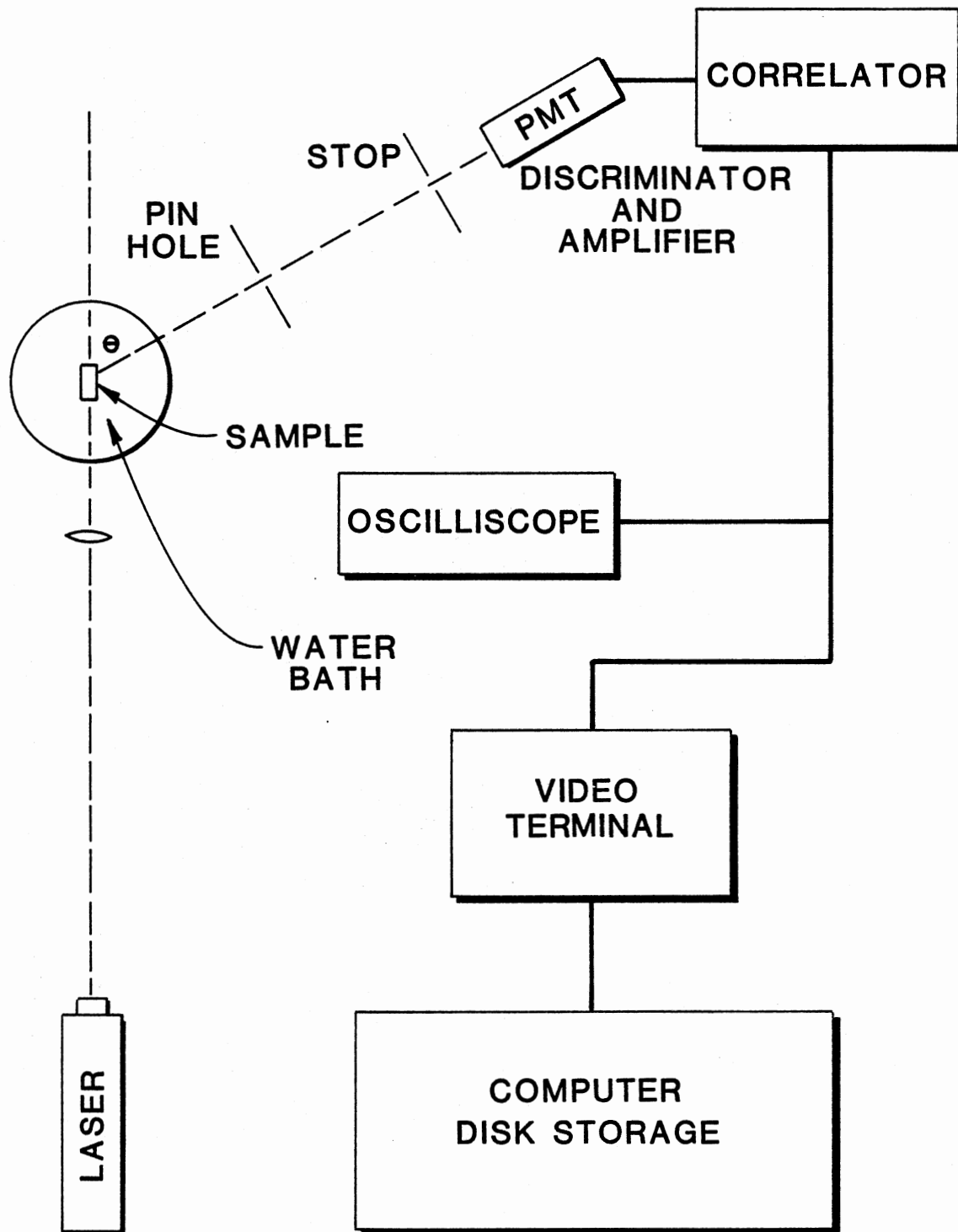


Figure 4. Diagram for DLS and SLS Apparatus

temperature was monitored and showed a maximum variation from  $24^{\circ}$  C to  $26.5^{\circ}$  C over the period when runs were taken.

## CHAPTER IV

### RESULTS

#### Undoped Sample

Figure 5 is a plot of  $S(q)$  for the undoped sample which displays a structure indicating that the scatterers are indeed interacting. This structure is typical of that seen for liquids (compare with Figure 3). The first (primary) peak,  $q_{\max} = 1.2 \times 10^5$  (1/cm), is indicative of a nearest neighbor distance of  $2\pi/q_{\max} = .52$  microns, and this is reasonable when compared to the mean particle separation estimated from the concentration by placing the particles at the lattice points of a simple cubic structure.

In order to test the validity of Equation 2.8 for this system, a method was needed to acquire the best value for the first cumulant,  $K_1$ , or the initial slope of the natural log of the time dependent part of the correlation function. The technique used was to take the dynamic run with the shortest sample time (2 or 5 microseconds), mask the first 2 points to avoid after-pulsing problems, and fit this data to a single cumulant fit.<sup>1</sup> At first all the points were fit, then half, quarter, and an eighth of the points walking in toward shorter times. These

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<sup>1</sup>A FORTRAN program called CORFIT written by Jim Appleman, Biochemistry Dept., OSU, which performs a non-linear least squares fit to the data was used for this single cumulant fit and also for later double exponential fits.



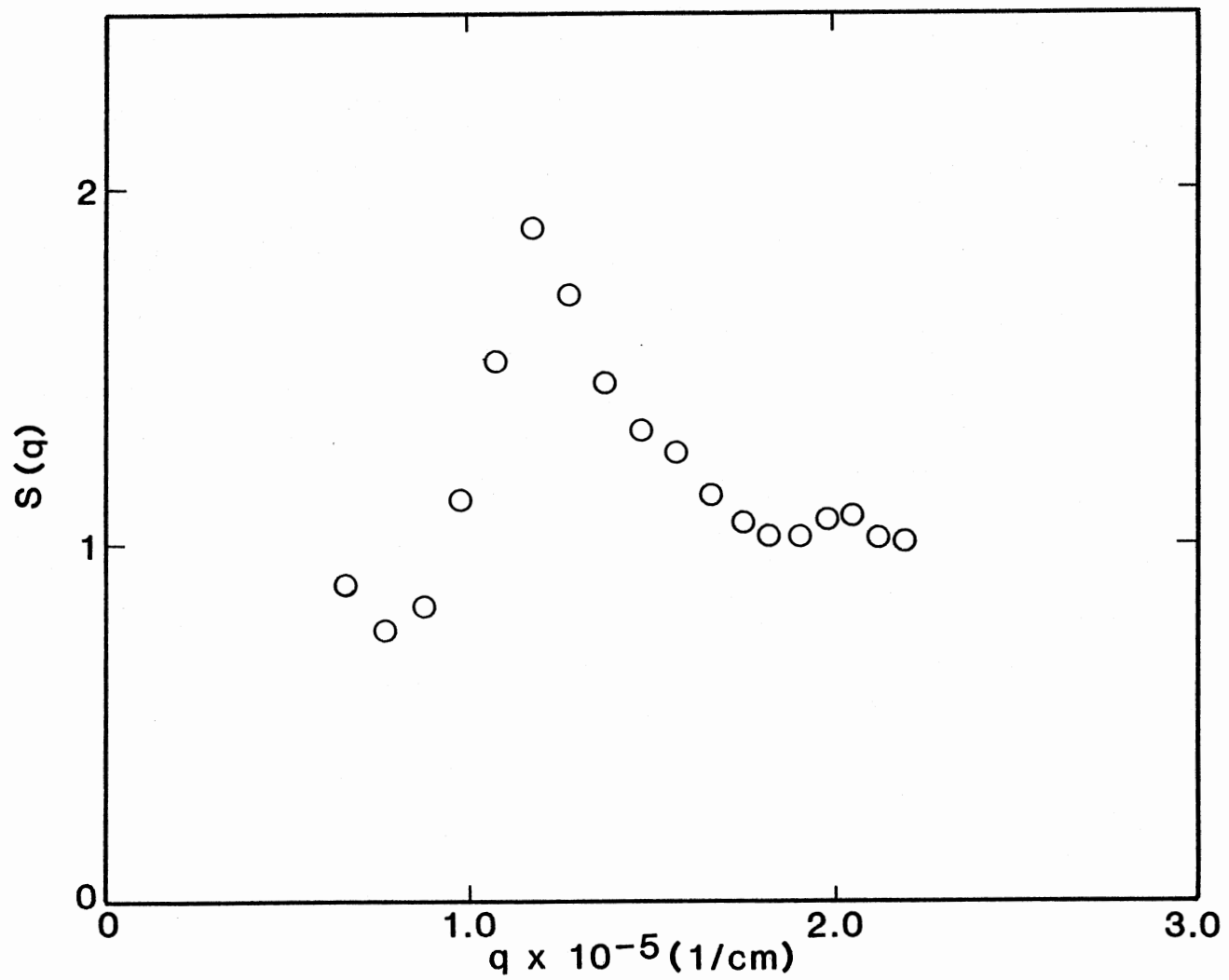


Figure 5. Structure Factor for the Undoped Sample

fitted values for  $K_1$  (4 for each run) were then plotted and extrapolated to  $t = 0$ . This extrapolation procedure was used for DLS runs on both doped and undoped samples to arrive at satisfactory values for the first cumulant in both cases.

For the undoped case, Figure 6 verifies the validity of the derivation of Equation 2.8, where a plot of  $q^2/K_1$  versus  $q$  almost exactly overlays the  $S(q)$  plot (Figure 5) when properly scaled. Also by estimating the value of  $K_1$  approached for large  $q$ , a value for the self-diffusion coefficient,  $D_0$ , can be obtained. For spherical particles the Stokes-Einstein relation gives

$$D_0 = k_B T / 6\pi\eta r$$

where  $k_B$  is Boltzman's constant,  $T$  is absolute temperature,  $\eta$  is the medium viscosity, and  $r$  is the particle radius. For a particle of .038 micron diameter,  $D_0$  is computed to be  $1.26 \times 10^{-7} \text{ cm}^2/\text{sec}$  compared to the estimated value of  $1.28 \times 10^{-7} \text{ cm}^2/\text{sec}$  which produces the dashed line in Figure 6.

Figure 7 is a plot of the natural log of the correlation function (doped sample at  $40^\circ$ ) versus  $q^2 t$ . This shows that there appears to be a constant long time effective diffusion rate. This behavior is evident in both samples. Pusey et al. have fitted for this long time decay,  $K_L$ , for interacting systems using a 2 exponential fit and found it to be usually around 3 times less than  $K_1$ , e.g. (5). This method was used to fit files of matched data<sup>2</sup> for both samples with

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<sup>2</sup>Several runs were made at each angle with different sample times. All these files for each angle were scaled and placed in a single file by a FORTRAN program, MATCH, which was also written by Jim Appleman of the Biochemistry Dept., OSU.

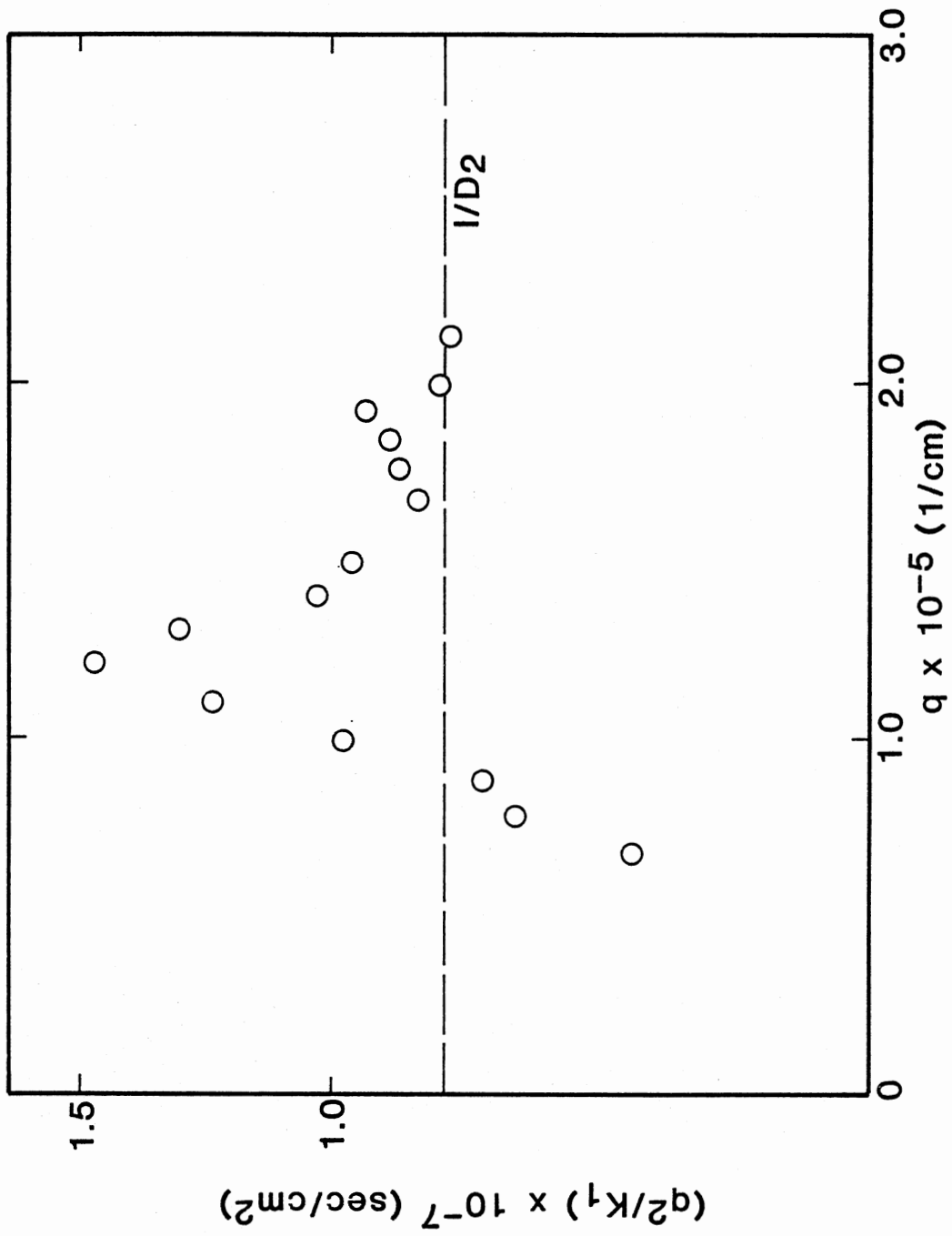


Figure 6.  $q^2/K_1$  Versus  $q$  for the Undoped Sample

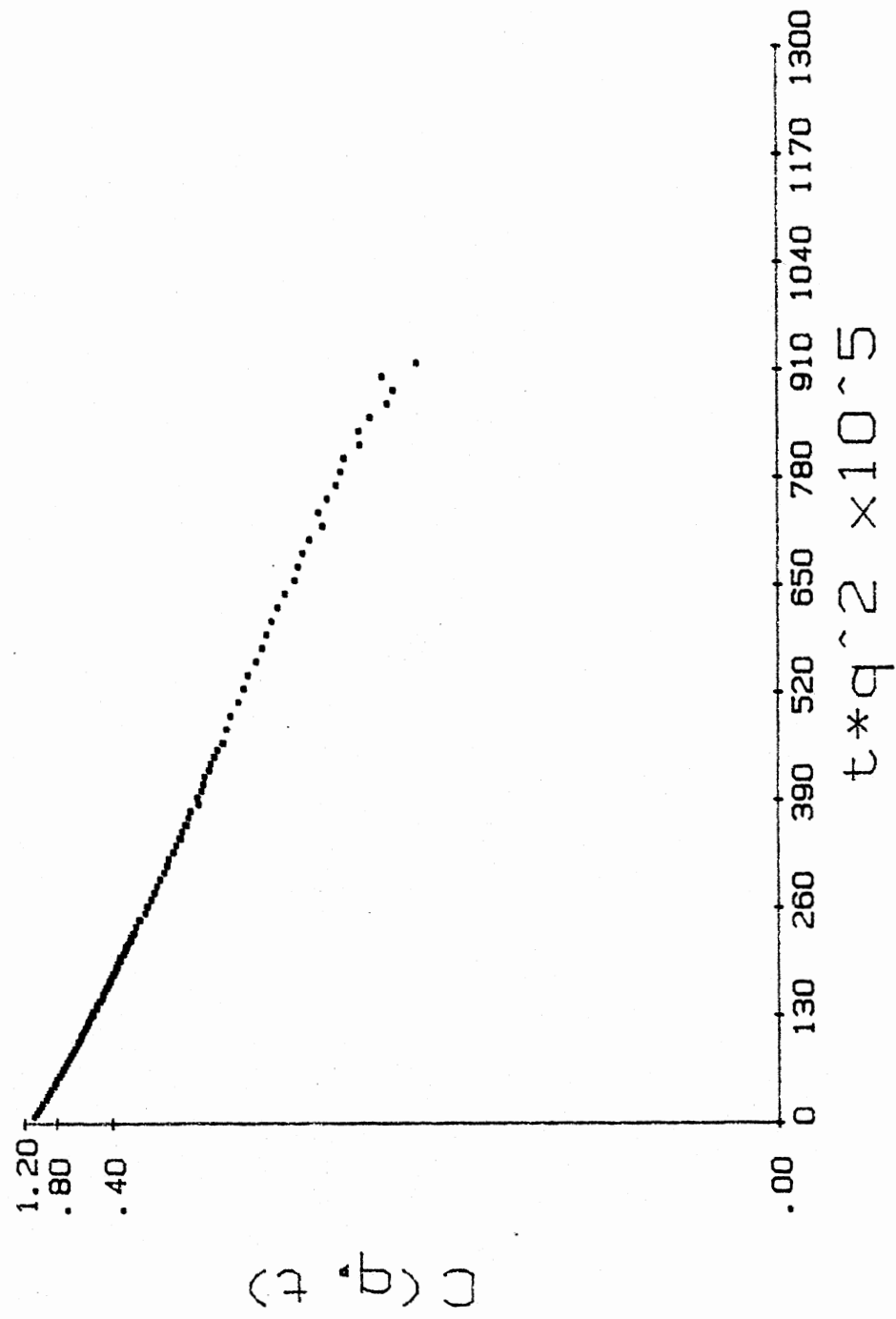


Figure 7.  $\ln(C(q,t))$  Versus  $q^2 t$  for Doped Sample at  $40^\circ$

results for the undoped sample shown in Figure 8. Matched files were used so that the entire correlation function (usually around 4 to 5 delay times) could be fit.

The control sample shows no surprises and confirms the relation, 2.8, which relates DLS and SLS. The more general version, Equation 2.9, will be tested in the analysis of the next section.

#### Doped Sample

Figure 9 shows  $S(q)$  for the doped sample which seems to display the liquid-like structure. If we interpret this as an actual liquid structure, the intensity peak,  $q_{\max} = 1.9 \times 10^5$  (1/cm), gives a nearest neighbor distance of  $2\pi/q_{\max} = .33$  microns. However, as mentioned earlier, when the particles are placed on a simple cubic lattice the concentrations used give a mean particle separation of only .69 microns for the small particles and 3.2 microns for the large particles.

A plot of  $q^2/K_1$  versus  $q$  (Figure 10) reproduces the structure, and by mimicking  $S(q)$  it seems to verify the relationship set forth in Equation 2.9. However, extrapolating to large  $q$  gives a self-diffusion rate,  $D_0 = 1.2 \times 10^{-7}$  cm<sup>2</sup>/sec, which corresponds to the smaller particles and is much too large for the larger particles. So if we accept 2.9 and assume scattering by large particles only, this places the  $l$  in the structure factor above the "primary" peak (see again Figure 9).

The long time single cumulant,  $K_L$ , again gives an effective diffusion rate around three times  $D_0$  with only slight  $q$  dependence (see Figure 11).

Next we shall discuss several possible explanations of the observed effects. However, we judge none to be entirely satisfactory.

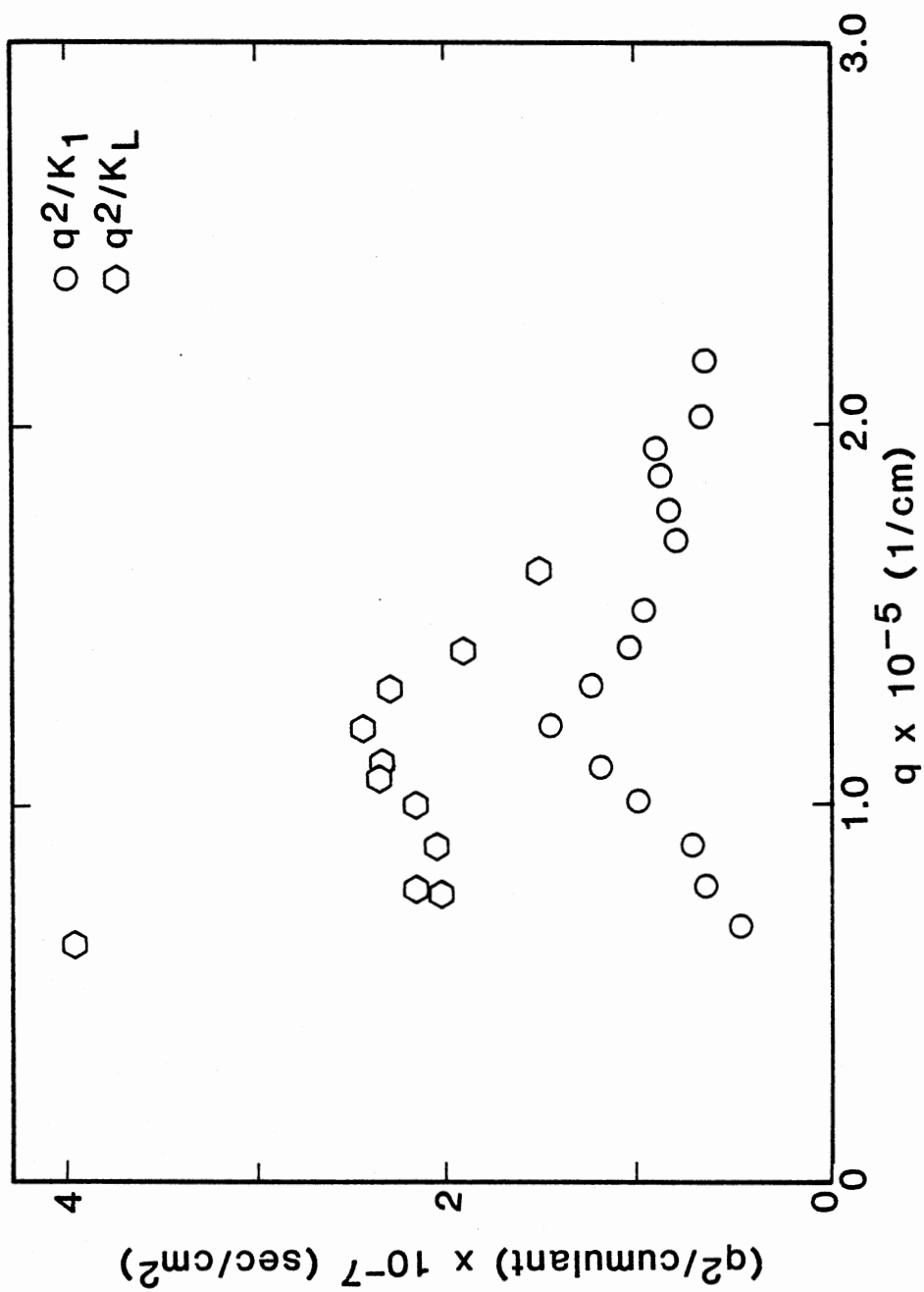


Figure 8.  $q^2/K_L$  Versus  $q$  for the Undoped Sample

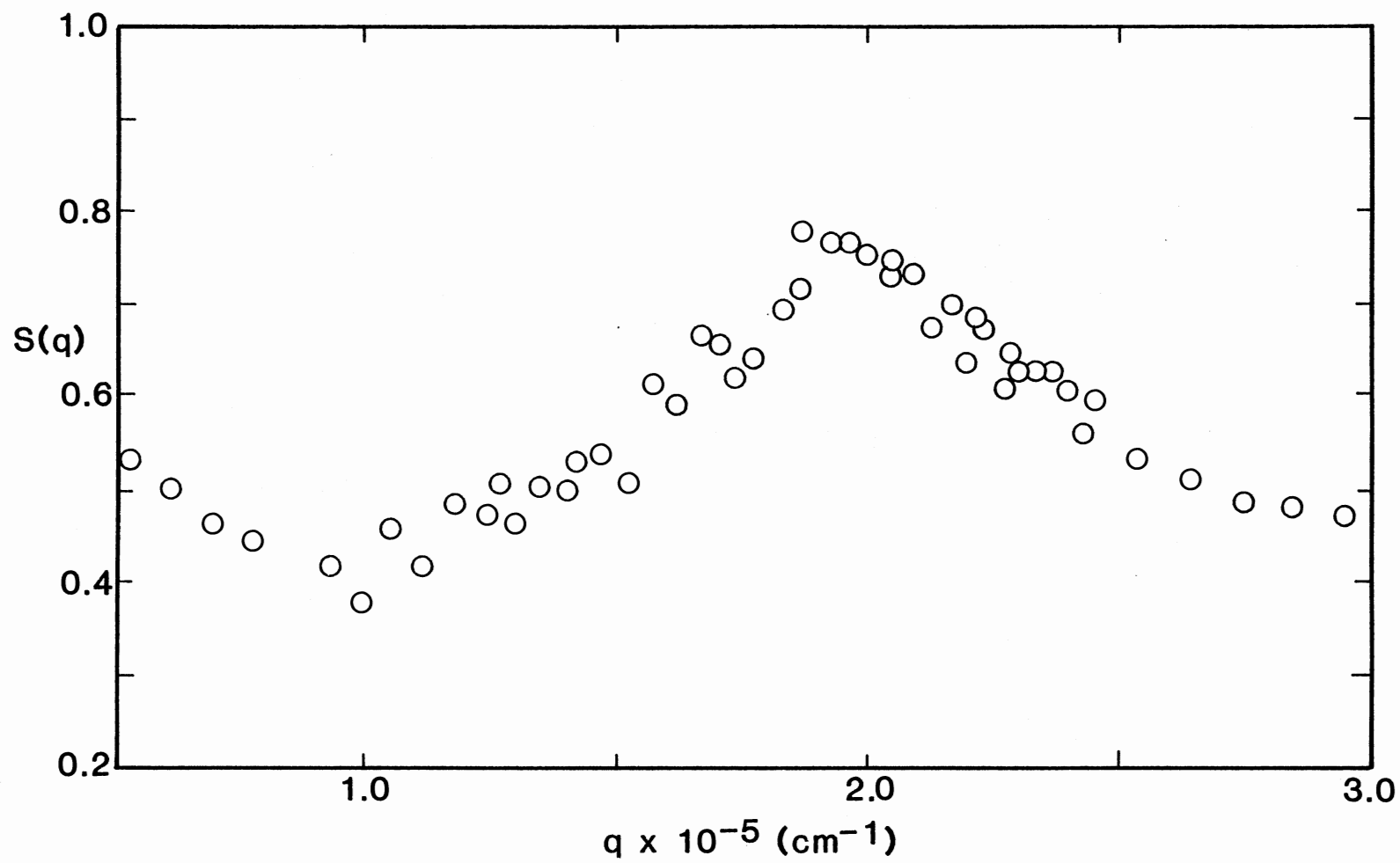


Figure 9. Structure Factor for the Doped Sample

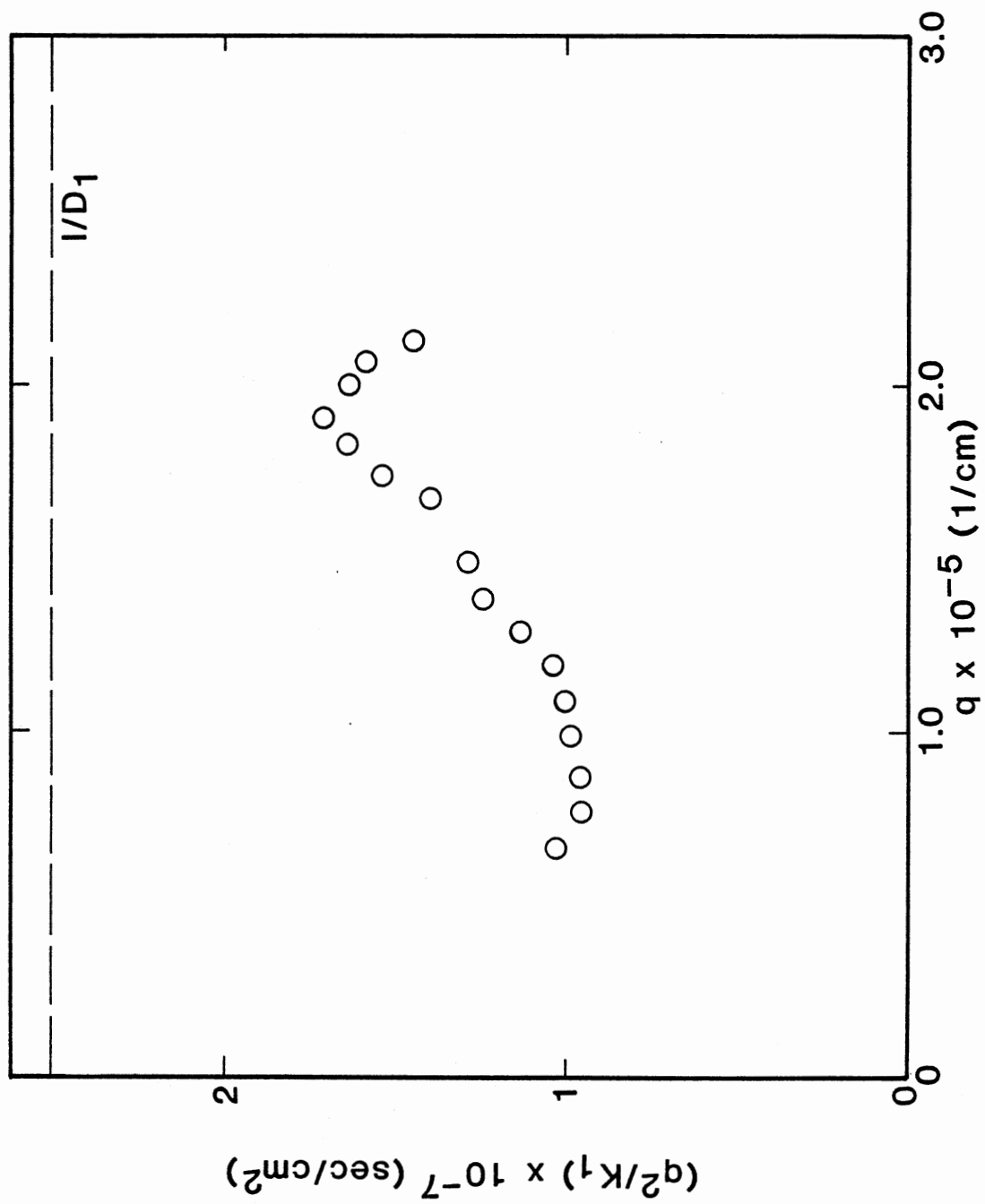


Figure 10.  $q^2/K_1$  Versus  $q$  for the Doped Sample



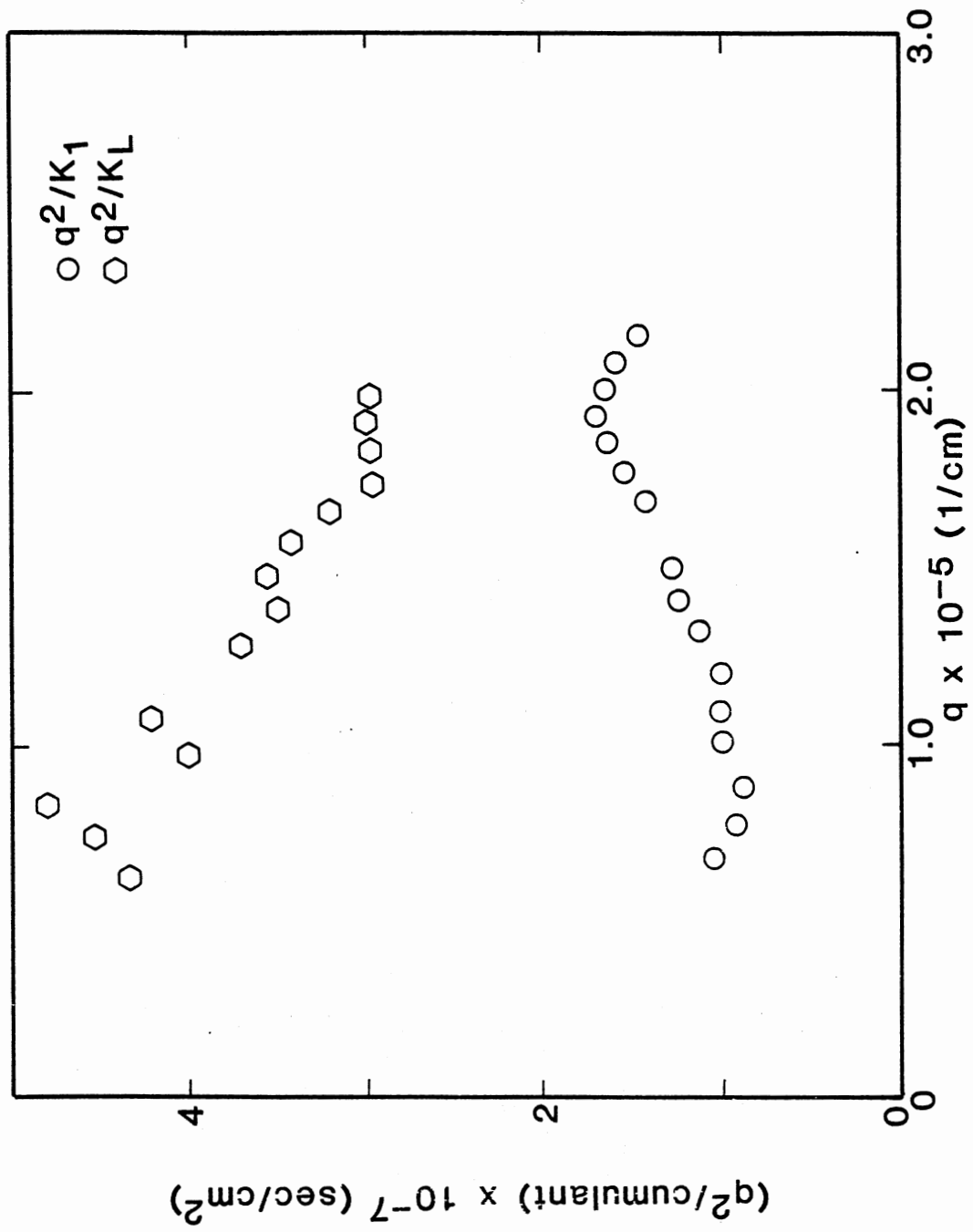


Figure 11.  $q^2/K_L$  Versus  $q$  for the Doped Sample

## CHAPTER V

### DISCUSSION

With the success of Equation 2.8 in the analysis of the undoped sample and the fact that the corresponding  $S(q)$  is still mimicked in the doped sample by  $q^2/K_1$  lends credibility to the more general relation 2.9, and its results on the dynamics of the doped sample. However, these results indicate a diffusion rate,  $D_0 = q^2/K_1$ , close to the self-diffusion rate calculated for the small particles using the Stokes-Einstein relation, but the structure seen should not be due to small particles since the majority of the light is scattered by the larger spheres. This fact is even visually apparent, because the doped sample scatters more light. The beam is much brighter through this sample and is comparable to a sample with an equal concentration of .109 micron particles alone. On the other hand, the larger particles should not be capable of producing such a rapid decay rate. In the following paragraphs we discuss in more detail these problems with application of the generalized cumulant description of colloidal mixtures.

We will begin by looking for a means of producing the structure seen in the doped sample's statics measurements. In the theory chapter we found there to be three terms contributing to the structure factor for a binary system. By examining each of these terms, we will attempt to determine the source of the structure shown in Figure 9 and mimicked by the dynamics in Figure 10.

Structure produced by the small particles,  $S_{22}$ , was predicted earlier by placing the spheres on a cubic lattice, and this gave a mean particle separation much larger than the nearest neighbor distance required to produce a peak at  $q = 1.9 \times 10^5$  (1/cm). But even if the larger particles are somehow crowding the smaller particles closer together, the smaller, .038 micron, particles don't scatter a large enough fraction (12%) of the total scattered intensity to produce structures of any significant magnitude in  $S(q)$ .

Since the large particles are at a concentration one hundredth that of the small ones, a uniform placement of the .109 micron spheres is much too far apart and would only show structure outside the range of  $q$  (at small  $q$ ) investigated. The small particles bunching the larger particles in close packed groups could give the structure seen, but the dynamics indicated by the first cumulant,  $K_1$ , is then too fast for .109 micron diameter particles.

This leaves correlations between the two different size particles,  $S_{12}$ , as a source of the structure. This particle separation,  $|r_1 - r_2|$ , could be small enough to produce a peak with the right  $q_{\max}$  if the larger spheres have less coulomb repulsion than the smaller ones (though both their actual surface charge is about 1000 electron charges).

Therefore the mixed correlation,  $S_{12}$ , seems a good guess to supply the proper results. By assuming most of the structure due to pairs of large particles is outside the range of  $q$  probed, we can essentially set  $S_{11}$  equal to 1. If we also assume the dopant particles have little effect on small particle pair correlations,  $S_{22}$  can be estimated from the undoped statics data. Using these suppositions and Equation 2.9,  $S_{12}$  can be found, and the results are shown in Figure 12. While the

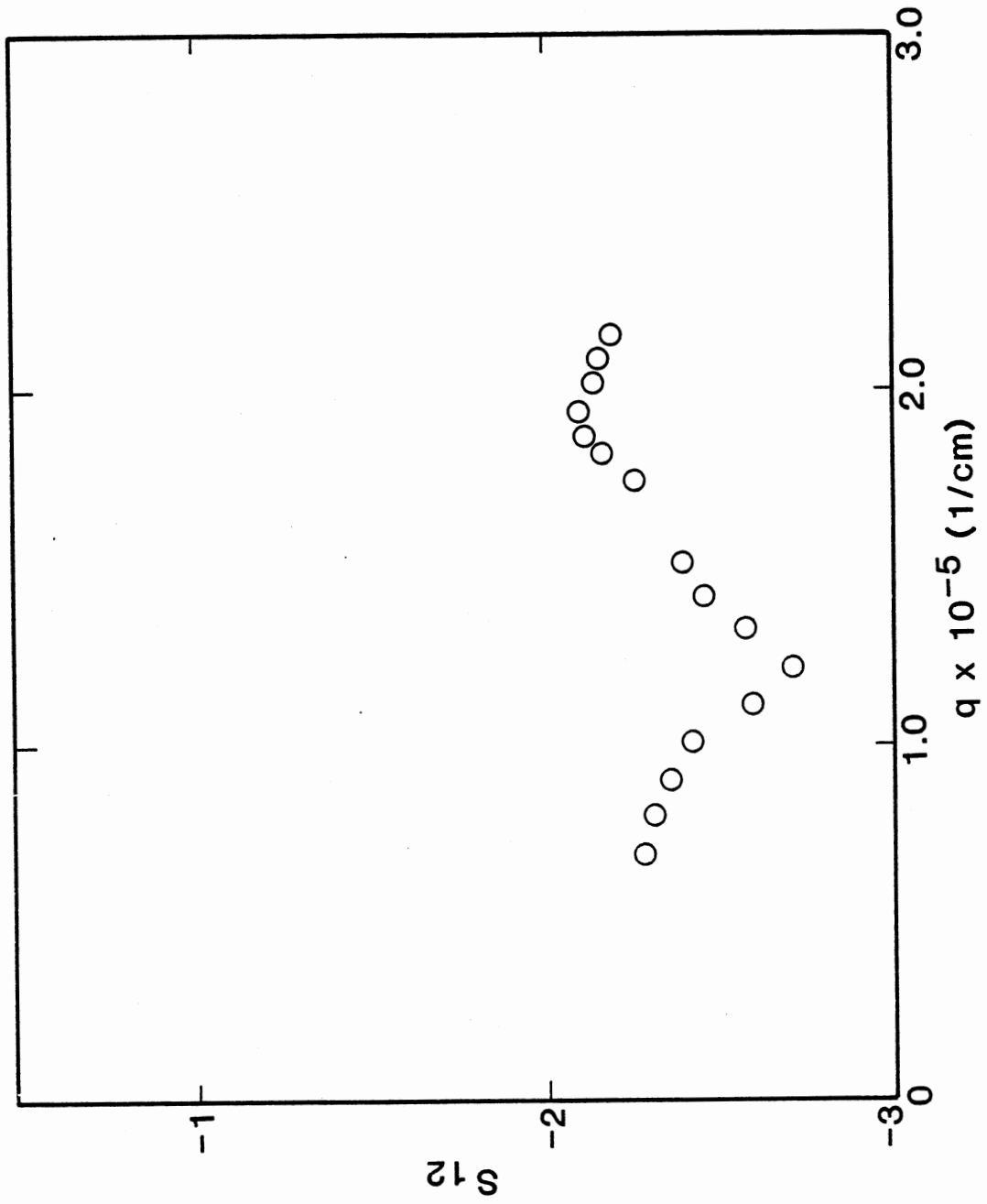


Figure 12. Plot of Estimated  $S_{12}$

nature of  $S_{12}$  is not obvious from its definition, the fact that the plot is always negative and does not approach 0 for large  $q$ , makes these results seem unreasonable.

Are there problems in the theory? This approach and the derivation of Equation 2.8 (Appendix) is not totally accepted, e.g. (6, 7). Yet, it works well for simple systems. Also the accuracy of 2.8 and its generalized version 2.9 depend on an estimate of where  $S(q) = 1$ , which could be misinterpreted by us from the plot, since the  $q$  range is limited. The derivation also assumes the system is in equilibrium. If the sample is a non-equilibrium (still evolving) system, then some time dependence should have been noticed. This is not the case for a year and a half. Nor did mild agitation seem to affect the structure either.

There is the possibility of a phase separated mixture such as oil and water. Since both size particles have around the same charge, they exert about the same pressure and could assume a single concentration where there are droplets of larger spheres in a sea of small ones. Here the separation is still not quite right and droplets can't diffuse any faster than the individual spheres. Other possible close packing situation such as aggregation also are not capable of giving the fast dynamics.

Multiple scattering which can give a fast initial decay should not be a problem for the low concentrations used.

The problem of fast dynamics could also be eliminated if somehow the presence of the smaller particles speeds up the larger particles; the small ones dragging the larger ones. This type of process has been seen in computer experiments by Ermak, e.g. (8). The closer packing

problem still remains.

There has been some recent work with colloidal alloys with latex spheres where certain concentration ratios for binary mixtures will produce complex crystalline superstructures, e.g. (9). Here pairs of close large particles widely separated in some uniform structure could be imagined to give the proper average separation, but our peak is broad, which is indicative of a weakly interacting liquid, and the rapid dynamics is still unexplained.

In conclusion we think we have found a system which is interesting because: it displays a structure which is not entirely understood, and it provides a possible challenge to the validity of current theory. For these reasons these systems deserve future work. The obvious immediate starting point would be to make more samples varying total concentration and the concentration ratio of the two species. Florescence tagging of the larger particles in some samples can be done to test whether or not self-diffusion is actually taking place. There needs to be further study of temperature dependence or effects of agitation on possible order-disorder transitions. Lastly, if the facilities were available, microscopy could be used to verify the existence of any alloy type structure, directly.

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## APPENDIX

### DERIVATION OF EQUATIONS 2.8 AND 2.9

The first cumulant can be extracted from the intermediate scattering function after normalization by evaluating the first time derivative at  $t = 0$ . Since

$$g^{(1)}(q, t) = F(q, t)/S(q) = \exp(-K_1 t + K_2 t^2/2! + \dots)$$

the first cumulant is given by

$$K_1 = -(1/S(q)) \left. \frac{\partial}{\partial t} F(q, t) \right|_{t=0}$$

To find the first cumulant for an interacting system, we need to define the intermediate scattering function in terms of the solution of the generalized diffusion equation (Equation 2.7), which can be written in an operator formalism.

$$\begin{aligned} P(\underline{R}, \underline{R}_0, t) &= D_0 \sum_i^N (\nabla_i^2 + \beta \nabla_i f_{ij}) P(\underline{R}, \underline{R}_0, t) \\ &= \tilde{O} \cdot P(\underline{R}, \underline{R}_0, t) \end{aligned}$$

For the two species case studied the operator takes the form

$$\tilde{O} = D_1 \sum_{k=1}^{n_1} (\nabla_k^2 + \beta \nabla_k f_{kj}) + D_2 \sum_{k=n_1+1}^N (\nabla_k^2 + \beta \nabla_k f_{kj})$$



with the particle number ( $n_1$  and  $n_2 = N - n_1$ ) and diffusion rates ( $D_1$  and  $D_2$ ) for each species. Here the fundamental solution,  $P(\underline{R}, \underline{R}_0, t)$ , is a function of the vector  $\underline{R} = (r_1, r_2, \dots, r_N)$  which represents all particle positions at time  $t$ . An initial configuration of  $\underline{R}_0 = (r_{10}, r_{20}, \dots, r_{N0})$  gives a fundamental solution evaluated at  $t = 0$  of

$$P(\underline{R}, \underline{R}_0, 0) = \delta(\underline{R} - \underline{R}_0) = \delta(r_1 - r_{10}) \delta(r_2 - r_{20}) \dots \delta(r_N - r_{N0})$$

Thus we define  $F(q, t)$  using this solution for an interacting system.

$$F(q, t) = (1/N) \sum_i^N \sum_j^N b_1 b_2 \langle \exp(i\underline{q} \cdot (\underline{r}_i - \underline{r}_{j0})) \rangle$$

$$F(q, t) = (1/N) \iint d\underline{R} d\underline{R}_0 \sum_i^N \sum_j^N b_1 b_2 \exp(i\underline{q} \cdot (\underline{r}_i - \underline{r}_{j0})) P(\underline{R}, \underline{R}_0, t)$$

$$\times \exp(-\beta\phi(\underline{R}_0)) / z$$

where  $\phi(\underline{R}_0)$  is the interaction potential,  $\frac{\partial}{\partial r_i} \phi(\underline{R}_0) = f_{ij}$ . The fact that the system is assumed to initially be in equilibrium is represented by multiplication by the factor  $\exp(-\beta\phi(\underline{R}_0)) / z$  with  $z = \int d\underline{R}_0 \exp(-\beta\phi(\underline{R}_0))$  and  $\exp(-\beta\phi(\underline{R}_0))$  being a solution to the differential equation (the equilibrium solution). Since a single time derivative operating on the solution to the differential equation is equivalent to the operator,  $\tilde{0}$ , taking the derivative of both sides of the above definition and moving the derivative inside the integral gives

$$\frac{\partial}{\partial t} F(q, t) \Big|_{t=0} = (1/N) \sum_i^N \sum_j^N b_1 b_2 \iint d\underline{R} d\underline{R}_0 \exp(i\underline{q} \cdot (\underline{r}_i - \underline{r}_{j0}))$$

$$\times (\exp(-\beta\phi(\underline{R}_0)) / z) \tilde{0} \delta(\underline{R} - \underline{R}_0)$$

After expanding the operator, we can integrate by parts and the resulting surface terms vanish since the delta functions are zero at infinite distance.

$$\begin{aligned} \frac{\partial}{\partial t} F(q, t) \Big|_{t=0} &= (1/N) \sum_i^N \sum_j^N b_i b_j \iint d\underline{R} d\underline{R}_0 \exp(i\underline{q} \cdot (\underline{r}_i - \underline{r}_j)) \\ &\times (-i\underline{q}) \cdot (\exp(-\beta\phi(\underline{R}_0)) / z) [D_1 \sum_{k=1}^{n_1} (\nabla_k + \beta f_{kj}) \\ &+ D_2 \sum_{k=n_1+1}^N (\nabla_k + \beta f_{kj})] \delta(\underline{R} - \underline{R}_0) \end{aligned}$$

If we again integrate by parts on the first term, the derivatives of the delta function are eliminated and the  $\underline{R}_0$  integration can be performed leaving

$$\begin{aligned} \frac{\partial}{\partial t} F(q, t) \Big|_{t=0} &= (1/N) \sum_i^N \sum_j^N b_i b_j \int d\underline{R} \exp(i\underline{q} \cdot (\underline{r}_i - \underline{r}_j)) (\exp(-\beta\phi(\underline{R})) / z) \\ &\times [D_1 \sum_{k=1}^{n_1} \delta_{ik} (-q^2 - i\underline{q} \beta f_{kj}) \\ &+ D_2 \sum_{k=n_1+1}^N \delta_{ik} (-q^2 - i\underline{q} \beta f_{kj})] \end{aligned}$$

Using the fact that  $\beta f_{kj} \exp(-\beta\phi) = \nabla_k \exp(-\beta\phi)$  and integrating by parts the second term only gives

$$\begin{aligned} \frac{\partial}{\partial t} F(q, t) \Big|_{t=0} &= (1/N) \sum_i^N \sum_j^N b_i b_j \int d\underline{R} (\exp(i\underline{q} \cdot (\underline{r}_i - \underline{r}_j)) / z) \\ &\times [D_1 \sum_{k=1}^{n_1} \delta_{ik} (-q^2 + a^2(1 - \delta_{jk})) \\ &+ D_2 \sum_{k=n_1+1}^N \delta_{ik} (-q^2 + q^2(1 - \delta_{jk}))] (\exp(-\beta\phi)) \end{aligned}$$

This reduces to

$$\begin{aligned} \frac{\partial}{\partial t} F(q, t) \Big|_{t=0} &= -(1/N) \sum_i^N \sum_j^N b_i b_j \int dR (\exp(iq \cdot (r_i - r_j)) / z) \\ &\times [D_1 \sum_{k=1}^{n_1} \delta_{ik} \delta_{ik} q^2 + D_2 \sum_{k=n_1+1}^N \delta_{ik} \delta_{jk} q^2] \\ &\times (\exp(-\beta\phi)) \end{aligned}$$

Since  $i$  and  $j$  must equal  $k$ , we can throw away two summations, and the exponential involving  $r_i - r_j$  vanishes to give

$$\begin{aligned} \frac{\partial}{\partial t} F(q, t) \Big|_{t=0} &= -(1/N) \int \frac{dR}{z} [D_1 \sum_{i=1}^{n_1} b_i^2 q^2 + D_2 \sum_{i=n_1+1}^N b_i^2 q^2] \\ &\times (\exp(-\beta\phi)) \end{aligned}$$

Since the remaining integral is simply  $z$  and the scattering fractions,  $b_i$ 's, depend only on the species, the sums reduce to give

$$\frac{\partial}{\partial t} F(q, t) \Big|_{t=0} = -(n_1 b_1^2 D_1 + n_2 b_2^2 D_2) q^2 / N$$

So, remembering that the first cumulant was our goal, we find

$$K_1 = - \frac{\partial}{\partial t} F(q, t) \Big|_{t=0} / S(q) = (n_1 b_1^2 D_1 + n_2 b_2^2 D_2) q^2 / S(q) N$$

This naturally reduces to

$$K_1 = D_0 q^2 / S(q)$$

for a single species system.

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