

The k dependence of the long-time diffusion in systems of interacting Brownian particles

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1979 J. Phys. A: Math. Gen. 12 L303

(<http://iopscience.iop.org/0305-4470/12/11/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 19:11

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

The k dependence of the long-time diffusion in systems of interacting Brownian particles

F Grüner and W Lehmann

Universität Konstanz, Fakultät für Physik, Bücklestraße 13, 7750 Konstanz, West Germany

Received 31 July 1979

Abstract. The short- and long-time diffusion coefficients in suspensions of charged polystyrene spheres were determined by means of photon correlation spectroscopy. Five different concentrations were measured. The results are discussed in a memory function formalism. It is shown that all concentrations and previously published data from different particles fit the same universal function.

1. Introduction

It is well known that in the presence of interaction between macromolecules the collective diffusion coefficient is affected considerably, both in its magnitude and in its time dependence. The best experimental tool to study this phenomenon is quasi-elastic light scattering. By this technique, Brown *et al* (1975) verified the short-time behaviour of the diffusion coefficient to be $D_0/S(k)$. D_0 is the free particle diffusion coefficient, $S(k)$ the static structure factor. This result was supported theoretically by Pusey (1975), who also observed (Pusey 1978) a long-time tail in the correlation function. The same results were published by Dalberg *et al* (1978).

Studying the concentration dependence of the long-time tail, we found that there are differences in the k dependence between short- and long-time behaviour of the correlation function. So we looked for a more detailed description of the dynamics of such systems of interacting Brownian particles. The timescales involved are defined by two collision times: τ_C , the typical time describing collisions between macromolecules and solvent molecules; and τ_{int} , the time describing collisions between the Brownian particles. Whereas τ_C is estimated to be of the order of 10^{-10} s, which is not covered by correlation spectroscopy, τ_{int} is governed by the motion of the particles and leads to a random interacting force varying on the same timescale as the diffusion itself. This force is most conveniently expressed in terms of a memory function in the generalised Langevin equation, leading to the following equation of motion for the correlation function $g(\tau)$:

$$\frac{d}{d\tau}g(\tau) = -\Omega(k)g(\tau) - \int_0^\tau dt M(t)g(\tau-t), \quad (1)$$

where

$$\Omega(k) = D_0k^2/S(k) = D_{\text{eff}}k^2, \quad (2)$$

and $g(\tau)$ is the particle density correlation function which is proportional to the field correlation function of the scattered light. The memory function $M(t)$ describes the dynamics of the particle interaction. It should be noted that the memory function introduces a non-Markov process which might affect the application of the Siegert relation. In the limit of very short times, however, the additional term in (1) vanishes, and for very long times the Markov approximation is applicable, so that in both limiting cases, $\tau \rightarrow 0$ and $\tau \rightarrow \infty$, the correct result should be reproduced by measuring the intensity correlation function and applying the Siegert relation.

The short-time diffusion coefficient is given by the first cumulant $\Omega(k)$ of $g(\tau)$. For the long-time diffusion coefficient D_L , we use the definition of the collective diffusion coefficient in the hydrodynamic limit given by Dieterich and Peschel (1979). If the Markov approximation is applicable for $k \neq 0$, D_L is given by

$$D_L = \lim_{\omega \rightarrow 0} \left(\frac{D_0}{S(k)} + \frac{M(k, -i\omega)}{k^2} \right), \quad (3)$$

where $M(k, z)$ is the Laplace transform of the memory function defined in equation (1).

2. Experimental details

From our experimental data we were able to determine the memory function at $\omega = 0$ for different particle concentrations as a function of k . The particles used were 0.045 μm radius polystyrene spheres supplied by Dow. They were suspended in water, which was de-ionised by a mixed-bed ion-exchange resin. Five different concentrations were prepared; the static structure factors are shown in figure 1. The dynamical measurements were performed using a 4000-channel correlator and analysed using a multiexponential-fit procedure (Provencher 1976). Both the static structure factors and the intensity correlations were corrected for multiple scattering as described by Grüner and Lehmann (1979). The corrected intensity correlation functions were then analysed using the Siegert relation and again fitting several exponentials.

We thus obtain an analytical representation of the field correlation function:

$$g^1(\tau) = \sum_i \alpha_i e^{-\Gamma_i \tau}, \quad \sum_i \alpha_i = 1. \quad (4)$$

From this model function the short- and long-time diffusion coefficients are easily calculated as the first cumulant

$$D_S k^2 = \sum_i \alpha_i \Gamma_i \quad (5)$$

and as the limit $\omega = 0$ of the Fourier transform of $g^1(\tau)$, the dynamic structure factor $S(k, \omega)$:

$$\lim_{\omega \rightarrow 0} S(k, \omega) = \frac{1}{\pi} \left(\frac{S(k)}{D_L(k, \omega = 0)k^2} \right) = \frac{1}{\pi} S(k) \sum_i \frac{\alpha_i}{\Gamma_i}, \quad D_L k^2 = \frac{1}{\sum_i \alpha_i / \Gamma_i}. \quad (6)$$

It should be emphasised that the long-time diffusion coefficient is not given by the long-time tail of the correlation function, but represents a sum over the total time evolution of the correlation function, in contrast to the interpretation of Pusey (1978)

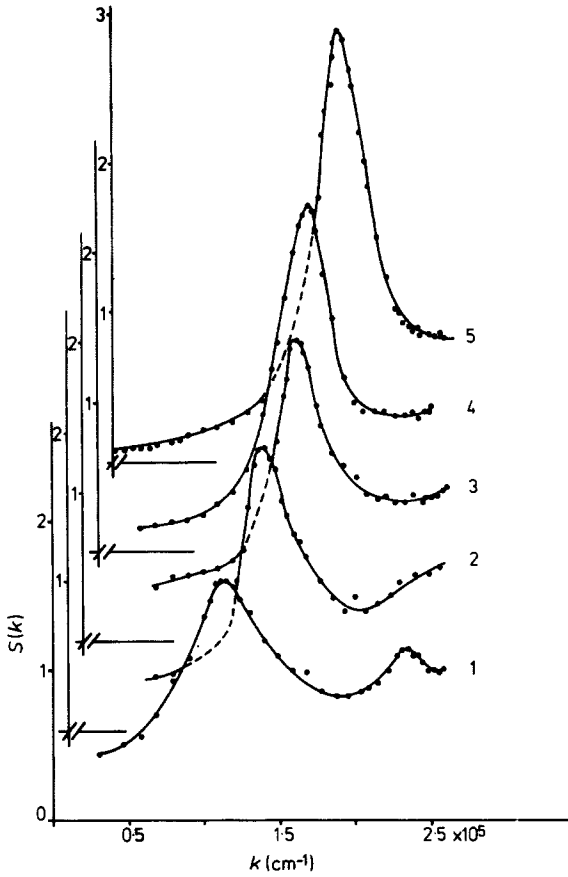


Figure 1. Measured static structure factors after correction for multiple scattering of the samples used in the experiments. Particle radius: 0.045 μm . Concentrations (10^{12} ml^{-1}): 1, 2.53; 2, 5.06; 3, 7.59; 4, 10.12; 5, 12.65.

and Dalberg *et al* (1978). From the measured quantities D_S and D_L , the memory function in the zero-frequency limit can be determined to be

$$M(k, \omega = 0) = (D_L - D_S)k^2. \tag{7}$$

We define a reduced memory function $M'(k, \omega = 0)$ by

$$M'(k, \omega = 0) = -\frac{M(k, \omega = 0)}{D_0 k^2 / S(k)} = \frac{D_S - D_L}{D_S}. \tag{7a}$$

This function is plotted in figure 2 over the reduced wavevector k/k_{max} , where k_{max} is the peak position in the static structure factor.

The surprising result is that all data from five different concentrations fit the same universal function $M'(k, \omega = 0)$. This leads to the conclusion that the shape of M' depends only on the shape of the interacting potential, and the concentration dependence enters only in k_{max} . In the same figure we have plotted the data of Pusey (1978)

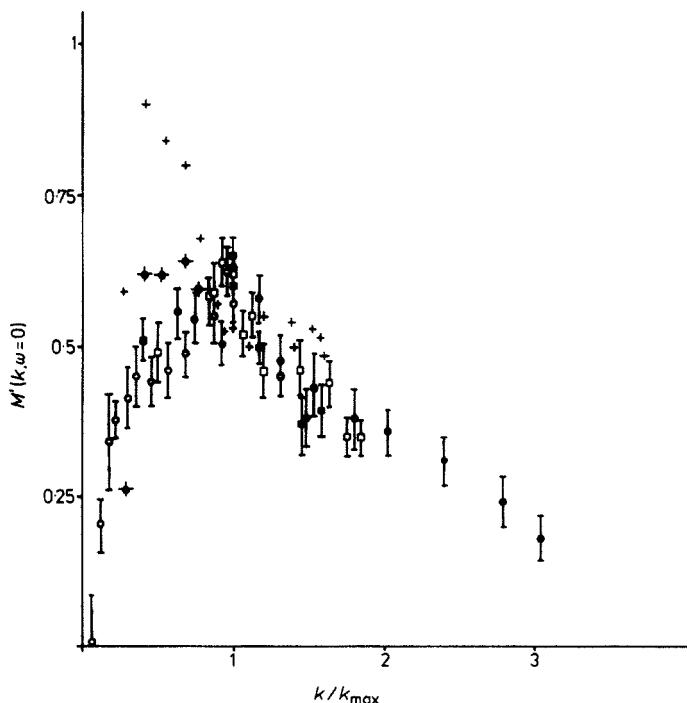


Figure 2. The reduced memory function $M'(k, \omega = 0)$: \bullet sample 1; \square sample 2; \blacksquare sample 3 + 4; \circ sample 5. Sample numbers refer to figure 1. Data from Pusey (1978), uncorrected (+) and corrected for multiple scattering (\blacklozenge).

obtained with particles of radius $0.025 \mu\text{m}$, analysed according to equations (5), (6) and (7a), once without correction for multiple scattering and once with a crude correction for multiple scattering, done in the following fashion. Taking the three corrected values given by Pusey, we have made a linear interpolation of the correction factor for D_{eff} . The result shows satisfactory agreement with our data. Thus we conclude that the particle size has a minor influence on the reduced memory function. It should be emphasised that our data for D_{eff} were always checked against the measured $S(k)$ to minimise the errors due to multiple scattering.

The memory function shows a pronounced peak at $k = k_{\text{max}}$, which is reasonable since for fluctuations on a lengthscale of the order of the mean particle distance the strongest influence of the interaction is expected. At larger k values, that is, shorter characteristic length, $M'(k, \omega = 0)$ dies off slowly with an approximate power law of $(k/k_{\text{max}})^{-1}$. It is only in this region where the simple picture of a particle fluctuating in a 'cage' of its neighbours holds. If the characteristic length of the fluctuation becomes larger, the interaction effects become stronger and the memory function increases, indicating that the system remembers the earlier state and needs a longer time to relax to equilibrium. At k values around and before the peak of $S(k)$ this picture no longer holds since the particles are indistinguishable. Thus, at characteristic lengths comparable with or greater than the mean interparticle distance, several particles are involved, and in the limit of very long fluctuations a mean over a large number of particles is involved. This is conveniently described by the mean field value $D_0/S(k)$, and thus the memory function has to vanish at $k \rightarrow 0$, which is indeed observed.

3. Conclusions

We have shown that in the long-time limit the dynamics of interacting Brownian particles may be described by the static structure factor $S(k)$, which gives the concentration dependence, and a memory function $M'(k, \omega = 0)$, independent of concentration and particle size, describing the dynamical aspects of the repulsive interaction potential.

An analysis of our data at finite frequencies is in progress and will be given later.

Acknowledgments

We are indebted to Professor Weber for encouraging support and to Dr Heß and Professor Klein for helpful discussions and valuable suggestions.

References

- Brown J C, Pusey P N, Goodwin J W and Ottewill R H 1975 *J. Phys. A: Math. Gen.* **8** 664
Dalberg P S, Bøe A, Strand K A and Sikkeland T 1978 *J. Chem. Phys.* **69** 5473
Dieterich W and Peschel J 1979 *Physica A* **95** 208
Grüner F and Lehmann W 1979 *J. Phys. A: Math. Gen.* **12** 0000
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