Long-time versus short-time behaviour of a system of interacting Brownian particles

1980 J. Phys. A: Math. Gen. 13 L5

(http://iopscience.iop.org/0305-4470/13/1/002)

J. Phys. A: Math. Gen., **13** (1980) L5–L10. Printed in Great Britain

LETTER TO THE EDITOR

Long-time versus short-time behaviour of a system of interacting Brownian particles

W Hess and R Klein

Universität Konstanz, Fakultät für Physik, D-7750 Konstanz, West Germany

Received 10 October 1979

Abstract. A Mori-type transport equation for the dynamical structure factor $S(\boldsymbol{k}, t)$ for a system of charged Brownian particles is solved in a mode–mode coupling approximation within the OCP model. The agreement with recent light scattering experiments on the difference between the long-time and the short-time decay of $S(\boldsymbol{k}, t)$ in systems of polystyrene spheres is satisfactory.

The dynamical properties of systems of interacting Brownian particles have been studied extensively in recent years, particularly by light scattering (Chu 1979). A widely used system consists of polystyrene spheres of several hundred Å radius in aqueous solution, where the spheres are highly charged. As a result there is a long-range interaction, which is in most cases the dominant interaction. Measurements of the static structure factor $S(\boldsymbol{k})$ yield liquid-like behaviour, characterised by a pronounced peak in $S(\boldsymbol{k})$ (Brown *et al* 1975). The dynamical properties, as revealed by light scattering, are determined by the autocorrelation function of the concentration fluctuations. This function, the dynamical structure factor $S(\boldsymbol{k}, t)$, has been found experimentally to be of non-exponential form. Therefore, the dynamics of this system cannot in general be represented by one effective diffusion coefficient. In particular, it was found that the long-time decay of $S(\boldsymbol{k}, t)$ is appreciably slower than the short-time decay, and that this difference in addition depends on k (Brown *et al* 1975, Pusey 1978, Dalberg *et al* 1978, Grüner and Lehmann 1979).

The purpose of this Letter is to show that the inclusion of memory effects in the dynamics can explain this behaviour. Starting from the Mori transport equation for $S(\boldsymbol{k}, t)$ the memory effects are treated in a simple mode–mode coupling approximation. The system of interacting charged particles is described by a one-component plasma (OCP) which enables us to calculate the memory function explicitly for all times and for small and large values of k, compared to $k_{\max}$, the position of the main peak in $S(\boldsymbol{k})$.

Starting from the Smoluchowski equation for the distribution function $P(\{\boldsymbol{R}_\alpha\}, t)$ for the coordinates $\boldsymbol{R}_\alpha$ of N interacting Brownian particles, one can derive a memory equation for the dynamical structure factor

$$S(\boldsymbol{k}, t) = \langle \delta c(\boldsymbol{k}, t) \delta c(-\boldsymbol{k}, 0) \rangle, \tag{1}$$

$\delta c(\boldsymbol{k}, t)$ being fluctuations around the mean concentration c. The average in (1) is defined by

$$\langle (\dots) \rangle = \int \mathrm{d}\{\boldsymbol{R}_\alpha\} (\dots) \exp\left[-\beta U_N(\{\boldsymbol{R}_\alpha\})\right] \left\{ \int \mathrm{d}\{\boldsymbol{R}_\alpha\} \exp\left[-\beta U_N(\{\boldsymbol{R}_\alpha\})\right] \right\}^{-1} \tag{2}$$

0305-4470/80/010005+06$01.00

where $U_N(\{\boldsymbol{R}_\alpha\})$ is the interaction potential. The Mori-type memory equation is, neglecting hydrodynamic interactions (Ackerson 1978, Dieterich and Peschel 1979),

$$\partial_t S(\boldsymbol{k}, t) = -\frac{D_0 \boldsymbol{k}^2}{S(\boldsymbol{k})} S(\boldsymbol{k}, t) + \frac{1}{S(\boldsymbol{k})} \int_0^t \mathrm{d}t' \, M(\boldsymbol{k}, t-t') S(\boldsymbol{k}, t') \qquad t > 0. \tag{3}$$

D_0 is the diffusion constant at infinite dilution, $S(\boldsymbol{k}) = (1/N)S(\boldsymbol{k}, t=0) \equiv 1 - ch(\boldsymbol{k})$ and the memory function is given by

$$M(\boldsymbol{k}, t) = \frac{1}{N} \langle F(\boldsymbol{k}, \{\boldsymbol{R}_\alpha\}) \exp[(1-\hat{P}_1)\hat{L}_0(\{\boldsymbol{R}_\alpha\})t] F(-\boldsymbol{k}, \{\boldsymbol{R}_\alpha\}) \rangle. \tag{4}$$

The random forces F are given by

$$F(\boldsymbol{k}, \{\boldsymbol{R}_\alpha\}) = (1-\hat{P}_1)\hat{L}_0^+(\{\boldsymbol{R}_\alpha\}) \delta c(\boldsymbol{k}). \tag{5}$$

The projection operator $\hat{P}_1$ projects a dynamical variable onto the subspace of concentration fluctuations $\delta c(\boldsymbol{k})$:

$$\hat{P}_1(\ldots) = \frac{1}{NS(\boldsymbol{k})} \langle (\ldots) \, \delta c(-\boldsymbol{k}) \rangle \, \delta c(\boldsymbol{k}) \tag{6}$$

and $\hat{L}_0(\{\boldsymbol{R}_\alpha\})$ is the Smoluchowski operator:

$$\hat{L}_0(\{\boldsymbol{R}_\alpha\}) = D_0 \sum_i \frac{\partial}{\partial \boldsymbol{R}_i} \left[\frac{\partial}{\partial \boldsymbol{R}_i} + \beta \left(\frac{\partial}{\partial \boldsymbol{R}_i} U_N(\{\boldsymbol{R}_\alpha\}) \right) \right]. \tag{7}$$

$\hat{L}_0^+$ denotes the Hermitian adjoint of $\hat{L}_0$.

The memory function, equation (4), is now calculated in a mode–mode coupling approximation. The whole subspace orthogonal to the subspace which is spanned by the concentration fluctuations $\delta c(\boldsymbol{k})$ is approximated by taking into account only bilinear products like $\delta c(\boldsymbol{k}) \, \delta c(\boldsymbol{k}')$. Defining a projector $\hat{P}_2$, which projects onto these bilinear products of concentration fluctuations, as

$$\hat{P}_2(\ldots) = \frac{V}{2N^2(2\pi)^3} \int \mathrm{d}^3k' \langle (\ldots) \delta c(-\boldsymbol{k}/2 + \boldsymbol{k}') \delta c(-\boldsymbol{k}/2 - \boldsymbol{k}') \rangle \times \frac{\delta c(\boldsymbol{k}/2 + \boldsymbol{k}') \delta c(\boldsymbol{k}/2 - \boldsymbol{k}')}{S(\boldsymbol{k}/2 + \boldsymbol{k}') S(\boldsymbol{k}/2 - \boldsymbol{k}')}, \tag{8}$$

our approximation consists of writing $1 - \hat{P}_1 = \hat{P}_2$ in equations (4) and (5). As a result, $M(\boldsymbol{k}, t)$ can be written as

$$M(\boldsymbol{k}, t) = \frac{V^2}{4N(2\pi)^6} \int \mathrm{d}^3k' \int \mathrm{d}^3k'' \frac{g(\boldsymbol{k}, \boldsymbol{k}') g(-\boldsymbol{k}, \boldsymbol{k}'')}{S(\frac{1}{2}\boldsymbol{k} - \boldsymbol{k}') S(\frac{1}{2}\boldsymbol{k} + \boldsymbol{k}') S(\frac{1}{2}\boldsymbol{k} - \boldsymbol{k}'') S(\frac{1}{2}\boldsymbol{k} + \boldsymbol{k}'')} \times C(\boldsymbol{k}, \boldsymbol{k}', \boldsymbol{k}'', t) \tag{9}$$

where

$$g(\boldsymbol{k}, \boldsymbol{k}') = -cD_0 \boldsymbol{k} \cdot [(\tfrac{1}{2}\boldsymbol{k} + \boldsymbol{k}') h(\tfrac{1}{2}\boldsymbol{k} + \boldsymbol{k}') + (\tfrac{1}{2}\boldsymbol{k} - \boldsymbol{k}') h(\tfrac{1}{2}\boldsymbol{k} - \boldsymbol{k}')] \tag{10}$$

$$C(\boldsymbol{k}, \boldsymbol{k}', \boldsymbol{k}'', t) = \frac{1}{N^2} \langle \delta c(\tfrac{1}{2}\boldsymbol{k} + \boldsymbol{k}') \delta c(\tfrac{1}{2}\boldsymbol{k} - \boldsymbol{k}') \exp[\hat{L}_0(\{\boldsymbol{R}_\alpha\})t] \, \delta c(-\tfrac{1}{2}\boldsymbol{k} + \boldsymbol{k}'') \delta c(-\tfrac{1}{2}\boldsymbol{k} - \boldsymbol{k}'') \rangle. \tag{11}$$

A Gaussian factorisation of $C(\boldsymbol{k}, \boldsymbol{k}', \boldsymbol{k}'', t)$ results in

$$M(\boldsymbol{k}, t) = \frac{1}{2c}\frac{k^3}{(2\pi)^3}\int \mathrm{d}^3x \frac{[g(\boldsymbol{k}, k\boldsymbol{x})]^2}{S(\tfrac{1}{2}\boldsymbol{k}-k\boldsymbol{x})S(\tfrac{1}{2}\boldsymbol{k}+k\boldsymbol{x})} R(\tfrac{1}{2}\boldsymbol{k}+k\boldsymbol{x}, t)R(\tfrac{1}{2}\boldsymbol{k}-k\boldsymbol{x}, t) \tag{12}$$

where $R(\boldsymbol{k}, t) = S(\boldsymbol{k}, t)/S(\boldsymbol{k})$.

In order to proceed, an explicit expression is needed for the statics of the system, described by $S(\boldsymbol{k})$. As a model of the system we use OCP, which should be an adequate description outside the immediate neighbourhood of $k = 0$. Denoting the charge on one macroparticle by Q and the charges on the counter-ions (of concentrations c_j) by q_j, the Debye length of the system is

$$\lambda = \left(\frac{4\pi\beta}{\epsilon}(Q^2c + q_jQc)\right)^{-1/2}. \tag{13}$$

But since $q_J \ll Q$, we have $\lambda = \lambda_B[1 + O(q_J/Q)]$ with

$$\lambda_B = \left(\frac{4\pi\beta}{\epsilon}Q^2c\right)^{-1/2} \equiv \kappa^{-1} \tag{14}$$

for the screening length of the macroparticles alone. For $k > \kappa q_J/Q$ we may therefore treat the counter-ions as a homogeneous background. The resulting system is an OCP, characterised by the plasma parameter $\Gamma = Q^2\beta/(\epsilon a)^{-1}$, where a is the mean distance between macroparticles and ϵ is the dielectric constant of the solvent.

The plasma is only capable of performing overdamped oscillations, since the starting point of the present treatment, the Smoluchowski equation, already assumes that the momenta of the Brownian particles have their equilibrium values due to the frequent encounters with the solvent particles. The overdamped plasma frequency is $\nu_p = M\omega_p^2/f_0 = D_0\kappa^2$, where $\omega_p^2 = 4\pi Q^2c(\epsilon M)^{-1}$ is the ordinary plasma frequency, M is the mass of a macroparticle and f_0 is the friction constant. The structure factor $S(\boldsymbol{k})$ of OCP can be written as

$$S(\boldsymbol{k}) = \frac{\boldsymbol{k}^2}{\kappa^2 + \boldsymbol{k}^2}Q(\boldsymbol{k}) \tag{15}$$

where the first factor is the Debye–Hückel expression, valid for $\Gamma \ll 1$. For very small k, $Q(\boldsymbol{k}) \approx 1$ for all Γ (Vieillefosse and Hansen 1975) whereas for $k > k_{max}$ we assume $Q(\boldsymbol{k}) = 1$. The function $Q(\boldsymbol{k})$ describes the peak structure of $S(\boldsymbol{k})$, but explicit forms of $Q(\boldsymbol{k})$ will not be needed in the limiting cases which we study.

We now evaluate $M(\boldsymbol{k}, t)$ for $k/k_{max} \ll 1$ and for $k/k_{max} \gg 1$ for OCP. In the first case ($k/k_{max} \ll 1$), $g(\boldsymbol{k}, k\boldsymbol{x}) = -D_0\boldsymbol{k}^2 + O(k^3)$ and

$$S(\tfrac{1}{2}\boldsymbol{k} - k\boldsymbol{x}) = \frac{k^2}{\kappa^2}(\tfrac{1}{4} - \hat{\boldsymbol{k}}\cdot\boldsymbol{x} + x^2) + O(k^3) \qquad \hat{\boldsymbol{k}} = \boldsymbol{k}/k. \tag{16}$$

For the functions $R(\boldsymbol{k}, t)$ in (12) the lowest-order approximation from equation (3) is used, in which memory effects are neglected, since M is at least $O(k^3)$. Therefore, in the integral, equation (2), $R(0, t) = \exp(-D_0\kappa^2|t|)$. The result is

$$M(\boldsymbol{k}, t) = M(\boldsymbol{k}, 0)\exp(-2D_0\kappa^2|t|) \tag{17}$$

$$M(\boldsymbol{k}, 0) = \tfrac{1}{16}D_0^2\kappa^4\frac{k^3}{c} \qquad k/k_{max} \ll 1. \tag{18}$$

With this expression for the memory function, the solution of equation (3) leads to a normalised dynamical structure factor consisting of two exponentials:

$$R(\boldsymbol{k}, t) = (1-\alpha(\boldsymbol{k}))\exp(-|t|/\tau_1)+\alpha(\boldsymbol{k})\exp(-|t|/\tau_2) \tag{19}$$

where the relaxation times are

$$\tau_{1,2}^{-1} = D_0\kappa^2\left[\tfrac{3}{2}\mp\tfrac{1}{2}(1+8\tilde{M}(k))^{1/2}\right] \tag{20}$$

and the weight of the two contributions to $R(\boldsymbol{k}, t)$ is determined by

$$\alpha(\boldsymbol{k}) = \tfrac{1}{2}[1-(1+8\tilde{M}(k))^{-1/2}]. \tag{21}$$

Furthermore:

$$\tilde{M}(k) = \frac{1}{D_0k^2}\int_0^\infty \mathrm{d}t\, M(\boldsymbol{k}, t) = \frac{2\pi}{16}ka\Gamma \tag{22}$$

gives the dependence on concentration, scattering angle and charge on the macroparticles The mean distance a between the macroparticles is related to $k_{\max}$. We use an empirical relation $a = 5{\cdot}25\, k_{\max}^{-1}$ (Grüner and Lehmann 1979). In figure 1 we have plotted $\ln R(\boldsymbol{k}, t)$ as a function of $\nu_p t$ for $\Gamma = 1$ for different values of $k/k_{\max} < 1$. The memory effects for $k \neq 0$ lead to a slower decay of $R(\boldsymbol{k}, t)$ with increasing t.

Let us now consider the opposite limiting case, $k \gg k_{\max}$. To lowest order in $(k/k_{\max})^{-1}$ we put $S(\boldsymbol{k}) = 1$ in (9) and (10). For $k \gg k_{\max}$ the correlation function $R(\boldsymbol{k}, t)$ to be used in (12) will be single-particle-like:

$$R(\boldsymbol{k}, t) = \exp(-D_0\boldsymbol{k}^2|t|) \qquad (k \gg k_{\max}) \tag{23}$$

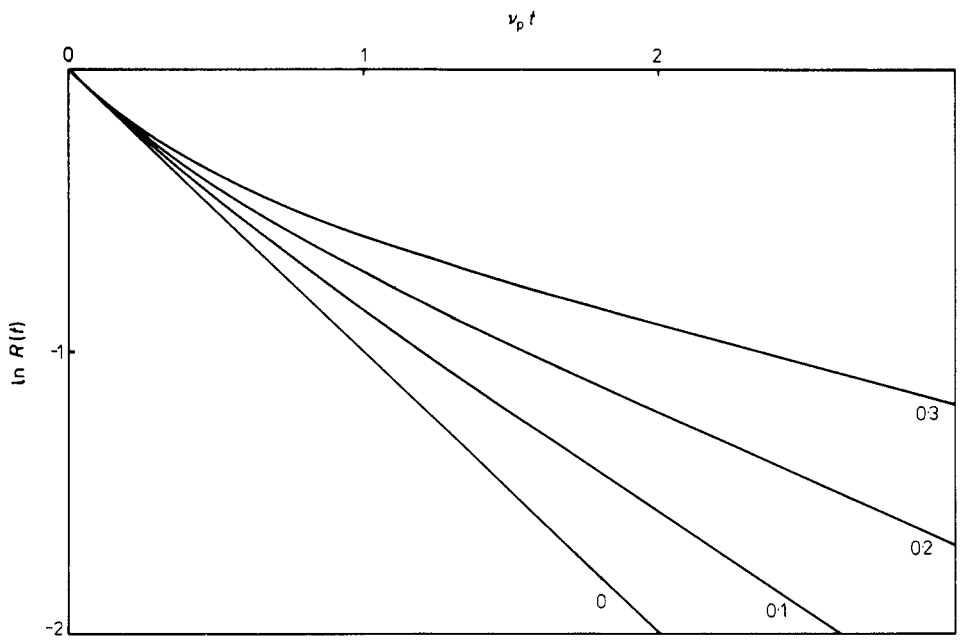

Figure 1. Reduced dynamical structure factor, equation (19), as a function of $\nu_p t$ for $k/k_{\max} = 0; 0{\cdot}1; 0{\cdot}2; 0{\cdot}3$ and $\Gamma = 1$.

so that, to lowest order in $(k/k_{\max})^{-1}$,

$$M(\boldsymbol{k}, t) = \frac{D_0^2}{c}\frac{k^3}{(2\pi)^3}\int \mathrm{d}^3x\{\boldsymbol{k}\cdot(\tfrac{1}{2}\boldsymbol{k}+k\boldsymbol{x})[1-S(\tfrac{1}{2}\boldsymbol{k}+k\boldsymbol{x})]\}^2 \exp[-(\tfrac{1}{2}+2x^2)D_0\boldsymbol{k}^2|t|]. \quad (24)$$

With the assumption $Q(k \gg k_{\max}) = 1$,

$$M(\boldsymbol{k}, t) = 12\pi\Gamma^2 D_0^2\frac{k^3}{a}\exp(-\tfrac{1}{2}D_0\boldsymbol{k}^2|t|)\frac{1}{(2\pi)^3}\int \mathrm{d}^3x\frac{(\frac{1}{2}+\hat{\boldsymbol{k}}\cdot\boldsymbol{x})^2}{(\frac{1}{4}+\hat{\boldsymbol{k}}\cdot\boldsymbol{x}+x^2)^2}\exp(-2x^2 D_0\boldsymbol{k}^2|t|). \quad (25)$$

It should be noted that this expression is not exponential in time; asymptotically it behaves as $t^{-3/2}\exp(-\frac{1}{2}D_0\boldsymbol{k}^2 t)$. From (25) one obtains

$$\tilde{M}(k) = \frac{1}{D_0 k^2}\int_0^\infty M(\boldsymbol{k}, t)\,\mathrm{d}t = 0{\cdot}86\,\Gamma^2(ka)^{-1} = 0{\cdot}16\,\Gamma^2(k/k_{\max})^{-1}. \quad (26)$$

In the present limit $\tilde{M}(k) \sim k^{-1}$, whereas $\tilde{M}(k) \sim k$ for $k \ll k_{\max}$ (equation (22)).

Defining a mean relaxation time for $R(\boldsymbol{k}, t)$ by

$$\tau(\boldsymbol{k})^{-1} = R(\boldsymbol{k}, 0)\left(\int_0^\infty \mathrm{d}t\,R(\boldsymbol{k}, t)\right)^{-1} \quad (27)$$

one finds, using (3) and (25), $\tau(\boldsymbol{k})^{-1} = D_0\boldsymbol{k}^2(1-\tilde{M}(k))$. Since, according to (26), $\tilde{M}(k) \sim k^{-1}$, $\tau(\boldsymbol{k})^{-1}$ approaches $D_0\boldsymbol{k}^2$ for $k \gg k_{\max}$, which is an *a posteriori* justification for equation (23).

Comparing the present results with experiments (Grüner and Lehmann 1979) we find the qualitative agreement concerning the k dependence of $\tilde{M}(k)$ for both limiting cases. For a quantitative comparison with experiment the value of the plasma parameter is needed. According to (19)–(22) the first cumulant for $k \to 0$ is given by $3\Gamma/a^2$. For the systems used in figure 2, more recent experiments yielded $\Gamma \approx 2$ (F Grüner and W Lehmann 1979 private communication). Using this value of Γ we have plotted our results (22) and (26). The agreement at large k is very satisfactory, whereas at low k the theoretical value is too large; $\Gamma = 1$ would be a better fit. Although

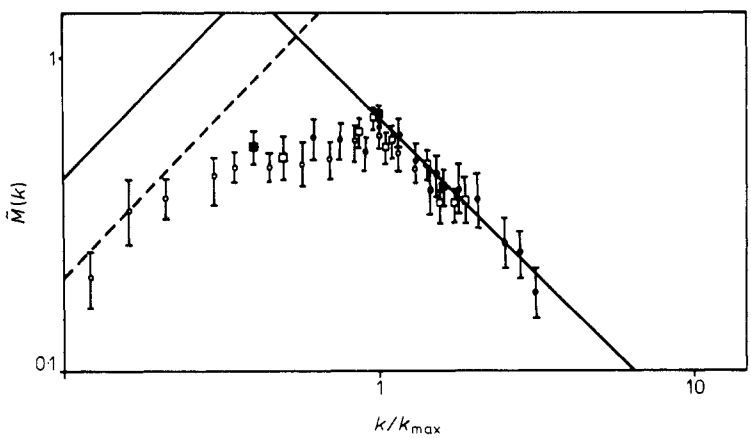

Figure 2. Comparison of theoretical results, equations (22) and (26), with experiments (Grüner and Lehmann 1979). Full lines correspond to $\Gamma = 2$ and broken line is equation (22) for $\Gamma = 1$.

these values for Γ still correspond to fairly strong coupling, they are surprisingly small for a system with a pronounced liquid-like structure factor. Possible reasons for this are the neglect of ladder corrections in our mode–mode coupling treatment and of the hard-core interaction. Ladder corrections are known to be important for a proper description of hydrodynamics. The hard core, on the other hand, will certainly contribute to the liquid-like structure, whereas our treatment of OCP uses point particles only. A further improvement is expected from an inclusion of hydrodynamic interactions.

Disregarding the complications just mentioned, we have shown that a simple mode–mode coupling treatment of overdamped OCP as a model for charged Brownian particles leads to non-exponential dynamical structure factors due to a coupling of the overdamped plasma oscillations to their first harmonics.

We would like to thank F Grüner and W Lehmann for stimulating discussions and providing us with their experimental results prior to publication.

References

Ackerson B J 1978 *J. Chem. Phys.* **69** 684
Brown J C, Pusey P N, Goodwin J W and Ottewill R H 1975 *J. Phys. A: Math. Gen.* **8** 664
Chu B 1979 *Phys. Scr.* **19** 458
Dalberg P S, Boe A, Strand K A and Sikkeland T 1978 *J. Chem. Phys.* **69** 5473
Dieterich W and Peschel J 1979 *Physica* **95A** 208
Grüner F and Lehmann W 1979 *J. Phys. A: Math. Gen.* **12** L303
Pusey P N 1978 *J. Phys. A: Math. Gen.* **11** 119
Vieillefosse P and Hansen J P 1975 *Phys. Rev.* A **12** 1106