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LETTER TO THE EDITOR

Fokker–Planck dynamics of interacting Brownian particles

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Abstract. Starting from an N -particle Fokker–Planck equation, the results for the concentration autocorrelation function are presented. It is shown that the corresponding memory function has the physical meaning of a $(k - \omega)$ -dependent longitudinal viscosity. A numerical mode–mode coupling calculation of the wavevector dependence of the longitudinal viscosity is found to be in good agreement with experimental results. Comparing the Fokker–Planck results with the corresponding Smoluchowski results show that the latter are only valid for small wavevectors or small interaction strength.

In recent years a number of dynamical light-scattering experiments have been performed on suspensions of charged spherical particles. For a detailed review of these experiments see Pusey (1980) and Pusey and Tough (1981). Characteristic features of results are a typical liquid-like static structure factor $S(k)$, which indicates short-range ordering, and a strongly non-exponential time behaviour of the concentration autocorrelation function, which does not result from polydispersity, and which depends on the wavevector. Since the discovery of the latter effect, the question of the cause of the deviation from a simple diffusion behaviour has been vividly discussed. Explanations have been sought in the frequency dependence of the hydrodynamic interaction (Berne 1977) and in the dynamics of counterions (Altenberger 1980), for example. But these possible explanations are ruled out by the fact that their typical relaxation frequencies are much larger than the experimentally determined first cumulant of the concentration autocorrelation function.

It has been shown that the first cumulant can be understood as the diffusion coefficient of a Brownian particle in the mean field of all other macroparticles (Pusey 1975, Ackerson 1976). The deviation from an exponential form must be due to processes which occur on a slower time scale. In an earlier publication we have shown that this effect may be understood as a viscoelastic relaxation of the longitudinal component of the stress due to the strong interactions between the particles (Hess 1981).

A numerical mode–mode coupling calculation of this effect (Hess and Klein 1981) showed a good qualitative agreement with experimental data (Grüner and Lehmann 1979). So far our starting point has always been a generalised diffusion equation for interacting Brownian particles, the generalised Smoluchowski or Kirkwood equation (SE). In this Letter I present the corresponding results obtained from a Fokker–Planck equation in phase space (FPE),

$$\begin{aligned} \partial f(\{\mathbf{r}, \mathbf{p}\}, t) / \partial t &= \hat{\mathcal{L}}^{\text{FP}} f(\{\mathbf{r}, \mathbf{p}\}, t), \\ \hat{\mathcal{L}}^{\text{FP}} &= -\sum_i \left(\frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i(\{\mathbf{r}\}) \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) + \zeta \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot \left(k_B T \frac{\partial}{\partial \mathbf{p}_i} + \frac{\mathbf{p}_i}{m} \right), \end{aligned} \quad (1)$$

where $f(\{\mathbf{r}, \mathbf{p}\}, t)$ is the N -particle distribution function in phase space, m is the mass of a Brownian particle, the \mathbf{p}_i are their momenta, $\mathbf{F}_i(\{\mathbf{r}\})$ is the interaction force on particle i due to the other Brownian particles, and ζ is the one-particle friction coefficient of a system without interactions. Hydrodynamic interaction is neglected here for simplicity and since it seems to be unimportant for the systems under consideration (Pusey and Tough 1981).

The purpose of this Letter is twofold. First, I want to show that, by starting from the Fokker–Planck equation, the viscoelastic explanation of the observed non-exponentiality in the concentration autocorrelation function gives a good quantitative agreement with experiment, over the whole range of scattering vectors. Second, because of these findings there arise strong doubts concerning the applicability of the Smoluchowski equation for systems with strong interactions outside the hydrodynamic limit. The SE has the form

$$\begin{aligned} \partial\rho(\{\mathbf{r}\})/\partial t &= \hat{L}^S \rho(\{\mathbf{r}\}, t), \\ \hat{L}^S &= D_0 \sum_i \frac{\partial}{\partial \mathbf{r}_i} \left(\frac{\partial}{\partial \mathbf{r}_i} - \beta \mathbf{F}_i(\{\mathbf{r}\}) \right), \quad \beta = (k_B T)^{-1}. \end{aligned} \quad (2)$$

Here $\rho(\{\mathbf{r}\}, t)$ is the configurational distribution function of N Brownian particles, and D_0 is the diffusion coefficient of a free particle, $D_0 = k_B T / \zeta$. The SE (2) can be derived from the FPE (1) by an expansion with respect to the spatial gradients $\partial/\partial \mathbf{r}_i$ (Murphy and Aguirre 1972), but alternatively the inverse friction coefficient can be used as an expansion parameter (Wilemski 1976, Titulaer 1978, Hess and Klein 1978). Although these derivations are only valid asymptotically, the widespread trust in the SE can be understood by the fact that for experimentally used frequencies and systems $\omega m / \zeta \ll 1$. Therefore the result of an expansion in ζ^{-1} seems to be reliable and the applicability of the SE has hardly ever been questioned. The first to calculate corrections to the SE were Wilemski and Titulaer. These authors showed that the correction terms are of the order of $((m/\zeta^2)\partial\mathbf{F}_i(\{\mathbf{r}\})/\partial\mathbf{r}_i)$; for a harmonic potential with a spring constant α this would be $(m\alpha/\zeta^2)$, for example. It follows that the corrections may be important for a system with strong interactions.

Instead of discussing the FPE and the SE in full generality directly, I take a more pragmatic point of view and compare certain correlation functions which can be calculated exactly from equations (1) and (2), respectively. The concentration autocorrelation function is

$$S(\mathbf{k}, t) = (1/N) \langle c(\mathbf{k}) \exp(\hat{L}^{\text{FP}} t) c(-\mathbf{k}) \rangle_0 \theta(t), \quad (3)$$

where $\langle (\dots) \rangle_0$ denotes a canonical expectation value and $c(\mathbf{k})$ the concentration fluctuations

$$c(\mathbf{k}) = \sum_i \exp(-i\mathbf{k} \cdot \mathbf{r}_i). \quad (4)$$

Applying the standard projection operator formalism to the time Fourier transform of $S(\mathbf{k}, t)$, we obtain the expression

$$S(\mathbf{k}, \omega) = \frac{S(\mathbf{k})}{i\omega + (k^2/m\beta S(\mathbf{k})) / (i\omega + \zeta/m + \eta_{\parallel}(\mathbf{k}, \omega)k^2/mc)}. \quad (5)$$

Here $S(\mathbf{k}) = S(\mathbf{k}, t=0)$, $c = N/V$ and

$$\eta_{\parallel}(\mathbf{k}, \omega) = (\beta/V) \langle \hat{\sigma}_{\parallel}(\mathbf{k}) [i\omega - \hat{Q}L^{\text{FP}}\hat{Q}]^{-1} \hat{\sigma}_{\parallel}(-\mathbf{k}) \rangle_0. \quad (6)$$

$\hat{Q} = 1 - \hat{P}$ and \hat{P} is a projection operator onto the space spanned by the concentration fluctuations $c(\mathbf{k})$ and the longitudinal gradients of particle current fluctuations,

$$\nabla \cdot \mathbf{j}(\mathbf{k}) = -i\mathbf{k} \sum_i \frac{\mathbf{p}_i}{m} \exp(-i\mathbf{k} \cdot \mathbf{r}_i). \quad (7)$$

$\hat{\sigma}_{\parallel}(\mathbf{k})$ may be interpreted as the longitudinal stress fluctuations of the Brownian particle system,

$$\begin{aligned} \mathbf{k}^2 \hat{\sigma}_{\parallel}(\mathbf{k}) &= -m\hat{Q}(L^{\text{FP}})^+ \nabla \cdot \mathbf{j}(\mathbf{k}) \\ &= \left(\sum_i i\mathbf{k} \cdot \mathbf{F}_i(\{\mathbf{r}\}) \exp(-i\mathbf{k} \cdot \mathbf{r}_i) - k_{\text{B}}T(S(\mathbf{k})^{-1} - 1)\mathbf{k}^2 c(\mathbf{k}) \right) \\ &\quad + \left(\sum_i \frac{(\mathbf{p}_i \cdot \mathbf{k})^2}{m} \exp(-i\mathbf{k} \cdot \mathbf{r}_i) - k_{\text{B}}T\mathbf{k}^2 c(\mathbf{k}) \right), \end{aligned} \quad (8)$$

where $(L^{\text{FP}})^+$ is the Hermitian adjoint of L^{FP} .

In the hydrodynamic limit equation (6) becomes the Kubo formula for the longitudinal intrinsic viscosity, and it can be shown that this identification can also be justified for arbitrary \mathbf{k} and ω . In order to do this, equation (6) is put in a different form. Using the formal properties $\hat{Q}^2 = \hat{Q}$, $\hat{P}^2 = \hat{P}$, $\hat{P}\hat{Q} = 0$ and the identity

$$[i\omega - \hat{Q}\hat{L}^{\text{FP}}]^{-1} = [i\omega - \hat{L}^{\text{FP}}]^{-1} - [i\omega - \hat{L}^{\text{FP}}]^{-1}\hat{P}\hat{L}^{\text{FP}}[i\omega - \hat{L}^{\text{FP}}]^{-1},$$

we obtain

$$\eta_{\parallel}(\mathbf{k}, \omega) = \frac{(\beta/N)\langle \hat{\sigma}_{\parallel}(\mathbf{k})[i\omega - \hat{L}^{\text{FP}}]^{-1}\hat{\sigma}_{\parallel}(-\mathbf{k}) \rangle_0}{1 + (\beta/N)\langle \nabla \cdot \mathbf{j}(\mathbf{k})[i\omega - \hat{L}^{\text{FP}}]^{-1}\hat{\sigma}_{\parallel}(-\mathbf{k}) \rangle_0}. \quad (9)$$

Using equation (8) and the identity

$$[i\omega - \hat{L}^{\text{FP}}]^{-1}\hat{L}^{\text{FP}} = -1 + i\omega[i\omega - \hat{L}^{\text{FP}}]^{-1},$$

this becomes

$$\eta_{\parallel}(\mathbf{k}, \omega) = \frac{(\beta/N)\langle \hat{\sigma}_{\parallel}(\mathbf{k})[i\omega - \hat{L}^{\text{FP}}]^{-1}\nabla \cdot \mathbf{j}(-\mathbf{k}) \rangle_0}{(\beta/N)\langle \nabla \cdot \mathbf{j}(\mathbf{k})[i\omega - \hat{L}^{\text{FP}}]^{-1}\nabla \cdot \mathbf{j}(-\mathbf{k}) \rangle_0}. \quad (10)$$

Both the numerator and the denominator now have the form of response functions. To see this, we introduce an external time-dependent potential into the FPE. This gives rise to an additional term in the FP operator,

$$\delta\hat{L}^{\text{FP}}(t) = -i(2\pi)^{-3} \int d^3k' U(\mathbf{k}', t) \sum_i \exp(i\mathbf{k}' \cdot \mathbf{r}_i) \mathbf{k}' \cdot \frac{\partial}{\partial \mathbf{p}_i}, \quad (11)$$

where $U(\mathbf{k}', t)$ are the Fourier components of the external potential. The linear response of an arbitrary quantity $a(\mathbf{k}, t) = \langle a(\mathbf{k}) \rangle_t$, which is the expectation value with the disturbed time-dependent distribution function, with respect to the external potential, becomes

$$a(\mathbf{k}, t) = \langle a(\mathbf{k}) \rangle_0 + \int_{-\infty}^t dt' \frac{\beta}{V} \langle a(\mathbf{k}) \exp[L^{\text{FP}}(t-t')] \nabla \cdot \mathbf{j}(-\mathbf{k}) \rangle_0 U(\mathbf{k}, t'). \quad (12)$$

Comparing this result with equation (10), we find

$$\eta_{\parallel}(\mathbf{k}, \omega) = \frac{\delta\hat{\sigma}(\mathbf{k}, \omega)}{\delta U(\mathbf{k}, \omega)} \bigg/ \frac{\delta \nabla \cdot \mathbf{j}(\mathbf{k}, \omega)}{\delta U(\mathbf{k}, \omega)} = \frac{\delta\hat{\sigma}(\mathbf{k}, \omega)}{\delta \nabla \cdot \mathbf{j}(\mathbf{k}, \omega)}. \quad (13)$$

Therefore the memory function $\eta_{\parallel}(\mathbf{k}, \omega)$ in equation (5) gives the response of the stress fluctuations to thermal fluctuations of the current gradients and has, for this reason, the meaning of a $(k - \omega)$ -dependent longitudinal viscosity.

For the frequency range of a light scattering experiment ($\omega < 10^6 \text{ s}^{-1}$), the systems in which we are interested are strongly overdamped, $\omega m/\zeta \ll 1$; therefore

$$S(\mathbf{k}, \omega) = \frac{S(\mathbf{k})}{i\omega + (D_0 k^2/S(\mathbf{k}))(1 + \eta_{\parallel}(\mathbf{k}, \omega)k^2/c\zeta)^{-1}}. \quad (14)$$

This must be compared with the corresponding result from the SE (Hess 1981),

$$S(\mathbf{k}, \omega) = \frac{S(\mathbf{k})}{i\omega + (D_0 k^2/S(\mathbf{k}))(1 - \eta_{\parallel}(\mathbf{k}, \omega)k^2/c\zeta)}, \quad (15)$$

where $\eta_{\parallel}(\mathbf{k}, \omega)$ has the same physical meaning as before, equation (13).

According to the two brackets in equation (8), the viscosity can be decomposed into an interaction term, a momentum term and two mixed terms. But the momentum relaxation occurs on a time scale of $O(m/\zeta)$ and therefore we keep only the interaction term. Applying now a mode-mode coupling approximation for this interaction term in the longitudinal viscosity yields the same result as obtained before, starting from the SE (Hess and Klein 1980, 1981).

$$\begin{aligned} \eta_{\parallel}(\mathbf{k}, t) &= \frac{k_B T}{(16\pi^3 k^4)} \int d^3 k' g(\mathbf{k}, \mathbf{k}')^2 S(\mathbf{k}_1, t) S(\mathbf{k}_2, t), \\ g(\mathbf{k}, \mathbf{k}') &= [\mathbf{k} \cdot \mathbf{k}_1 (S(\mathbf{k}_1) - 1) + \mathbf{k} \cdot \mathbf{k}_2 (S(\mathbf{k}_2) - 1)] / (S(\mathbf{k}_1) S(\mathbf{k}_2)), \\ \mathbf{k}_{1,2} &= \mathbf{k}/2 \pm \mathbf{k}'. \end{aligned} \quad (16)$$

Equations (14) and (16) are a closed set of nonlinear equations for the determination of $S(\mathbf{k}, t)$ or $S(\mathbf{k}, \omega)$, respectively. A lowest-order approximation is obtained if we use in (16) the mean field approximation

$$S(\mathbf{k}, t) = S(\mathbf{k}) \exp(-D_0 k^2 t/S(\mathbf{k})) \theta(t). \quad (17)$$

In this approximation $\eta_{\parallel}(\mathbf{k}, t)$ has been calculated analytically for specific models for $S(\mathbf{k})$, and numerically, using an experimental result for $S(\mathbf{k})$ (Hess and Klein 1980, 1981). The non-exponentiality in the experimental $S(\mathbf{k}, t)$ has been analysed by Grüner and Lehmann (1979) by the relative deviation between the inverse first cumulant and a mean relaxation frequency,

$$\begin{aligned} M(\mathbf{k}) &\equiv (\mu_1(\mathbf{k}) - \nu(\mathbf{k})) / \mu_1(\mathbf{k}), \\ \mu_1(\mathbf{k}) &= -\frac{\partial}{\partial t} \ln S(\mathbf{k}, t)|_{t=0}, \quad \nu(\mathbf{k}) = S(\mathbf{k}) / \int_0^\infty dt S(\mathbf{k}, t). \end{aligned} \quad (18)$$

Comparing the quantity $M(\mathbf{k})$ with equations (14) and (15), we find

$$M(\mathbf{k}) = \begin{cases} \frac{\eta_{\parallel}(\mathbf{k}, \omega=0)k^2/c\zeta}{1 + \eta_{\parallel}(\mathbf{k}, \omega=0)k^2/c\zeta} & \text{from the FPE,} \\ \eta_{\parallel}(\mathbf{k}, \omega=0)k^2/c\zeta & \text{from the SE.} \end{cases} \quad (19a) \quad (19b)$$

Figure 1 shows a comparison of the mode-mode coupling calculation of $\eta_{\parallel}(\mathbf{k}, \omega=0)k^2/c\zeta$, equations (16) and (17), using the experimental $S(\mathbf{k})$, with the corresponding $M(\mathbf{k})$ from the FPE (19a), and the experimental data. There is a good agreement

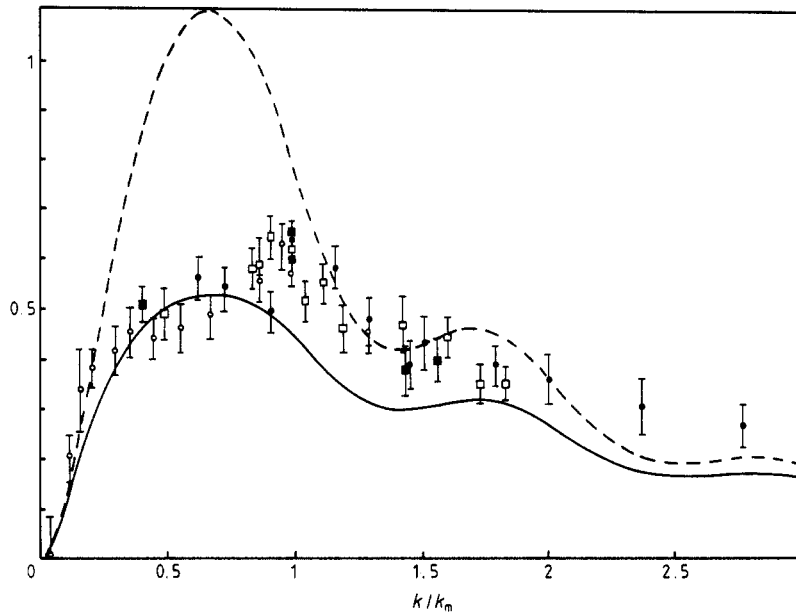


Figure 1. Non-exponentiality factor $M(\mathbf{k})$, as defined in equations (18) and (19a), and normalised longitudinal viscosity $\eta_{\parallel}(\mathbf{k}, \omega = 0)k^2/c\zeta$ in comparison with the experimental results for $M(\mathbf{k})$ (Grüner and Lehmann 1979). Full curve: theoretical $M(\mathbf{k})$; broken curve: $\eta_{\parallel}(\mathbf{k}, \omega = 0)k^2/c\zeta$.

between theory and experiment for the $M(\mathbf{k})$ from the FPE. The agreement with $M(\mathbf{k})$ from the SE is only satisfactory at small and large k , where the effect is small. This is easily understood from equations (19a,b): the results from the FPE and the SE coincide if $\eta_{\parallel}(\mathbf{k}, \omega = 0)k^2/c\zeta \ll 1$.

It was said in the beginning that the SE can be derived from the FPE by an expansion with respect to the spatial gradients and with respect to the inverse friction coefficient. Comparing now the exact results for $S(\mathbf{k}, \omega)$ from the FPE, equation (5), with the corresponding result from the SE, equation (15), we find that both indeed become identical for $k \rightarrow 0$. But for arbitrary k there are two conditions to obtain coincidence between equations (5) and (15), $\omega m/\zeta \ll 1$, which leads from equation (5) to (14), and $\eta_{\parallel}(\mathbf{k}, \omega)k^2/c\zeta \ll 1$. The first condition can always be fulfilled by choosing suitable experimental conditions. For the light scattering experiments on polystyrene latexes, for example, it is well fulfilled. But the second condition depends on the value of the generalised longitudinal viscosity, which is an intrinsic property of the system under consideration. It is determined by the interaction strength, by concentration, temperature, etc. For our example, the highly charged polystyrene latexes, both the numerical calculation as well as the experimental data show for a wavevector $k = k_m$ (k_m is the wavevector where $S(\mathbf{k})$ has its first maximum) that $\eta_{\parallel}(k_m, \omega = 0)k_m^2/c\zeta \approx 1.1$. Therefore the second condition is not fulfilled and equation (14), not the SE result (15), is the appropriate form of $S(\mathbf{k}, \omega)$ for these systems.

Since the SE is derived from the FPE the FPE must be considered as superior. A discrepancy of results obtained from both equations therefore indicates a deficiency of the SE. My conclusion is that the SE is not suited to describe systems with strong interaction outside the hydrodynamic regime, on a spatial length scale of the order of the correlation length.

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