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On the Gaussian approximation in colloidal hard sphere fluids

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We study the behaviour of the self-intermediate scattering function and self-van Hove correlation function for quasi-two-dimensional colloidal hard sphere fluids at a range of area fractions. We compute these functions first directly from the particle coordinates and secondly from the mean squared displacement *via* the Gaussian approximation. This allows us to test the validity of this approximation over a range of length and time scales, where we find that the Gaussian approximation holds if the hydrodynamic limits are appropriately probed. Surprisingly, only small deviations from Gaussian behaviour are seen at intermediate times, even for dense fluids. We next consider these deviations from Gaussian behaviour firstly *via* the non-Gaussian parameter and secondly by considering the relaxation times of the intermediate scattering function. From these measurements we develop a scaling relation in order to directly determine the combinations of wavevectors and times at which the non-Gaussian behavior is seen. This allows for the clear identification of the hydrodynamic regimes and thus provides new insight into the crossover between long- and short-time self-diffusion.

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1 Introduction

Scattering techniques have long played an important role in the study of complex fluids, where they have been used to probe a wide range of phenomena related to the structure and dynamics of systems such as colloidal fluids, polymer solutions or proteins in membranes.^{1–8} In scattering experiments, the central dynamic quantity is the intermediate scattering function (ISF), $F(k, t)$ with k the wavevector, which is directly related to the fluctuations in the intensity of the scattered light as a function of time.⁹ $F(k, t)$ can be split into two components, which describe either the self or collective behaviour. The calculation of the self-part, $F_s(k, t)$, allows a number of other properties to be determined indirectly, most importantly the mean squared displacement (MSD), $\delta r^2(t)$, and the self-diffusion coefficients.

The conversion between the self-ISF obtained from scattering measurements and the MSD requires the use of the Gaussian approximation.^{10,11} This assumes that the self-ISF is Gaussian and related to the MSD as

$$F_s(k, t) = \exp(-\delta r^2(t)k^2/2d), \quad (1)$$

with d the dimensionality. Eqn (1) is known to hold in a variety of circumstances, including in the description of the motion of a harmonic oscillator¹² and that of a system of diffusing particles,¹³ and has been used to interpret results from a wide range of experimental techniques,¹⁴ *e.g.* inelastic neutron scattering⁶ and spin-echo spectroscopy.⁵ For many systems, however, the self-ISF is seen to be Gaussian only for certain combinations of wavevectors and timescales, which implies that eqn (1) is only valid in certain regimes. In the case of diffusion this regime is termed the hydrodynamic limit.¹¹ Identifying these regimes is far from trivial, but crucial for the correct interpretation of results. Thus, efforts to characterise and quantify the deviations from Gaussian behaviour, and therefore to probe these regimes, are of widespread importance.

For colloidal diffusion in particular, single particle transport is diffusive at both short and long times. As such, two diffusion coefficients may be defined, with two corresponding hydrodynamic limits. These are associated with Gaussian behaviour as

$$F_s(k, t) = \exp(-D_i k^2 t), \quad i = S, L, \quad (2)$$

where D_i either corresponds to the short-time self-diffusion coefficient, D_s , or the long-time self-diffusion coefficient, D_L .¹⁵ For diffusion, the use of the Gaussian approximation arises from the fact that particles exhibit a random walk, characterised by a sequence of small independent displacements with zero mean, such that the central limit theorem applies. For short-time diffusion, the hydrodynamic limit is associated with length and time scales that are large compared to the characteristic scales

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Fig. 2 The variation of the self-van Hove function, $G_s(x,t)$, with time at (a) $\phi = 0.08$ and (b) $\phi = 0.66$. Symbols show $G_s(x,t)$ computed from eqn (6) and lines are calculated from the MSD using the Gaussian approximation, eqn (7). Values of t in (b) apply to both panels. (c) The variation in the non-Gaussian parameter, $\alpha_2^{(D)}(t)$, with ϕ . The dashed vertical orange line indicates the time at which $\alpha_2^{(D)}(t)$ for $\phi = 0.66$ reaches a maximum.

information about the lengthscale dependence of the deviations from Gaussian behaviour.

To address the relationship between Fickian diffusion and the Gaussian approximation,^{14,21} we show in Fig. 1c a straight line with a gradient corresponding to the self-diffusion coefficient at long times, which appears to be in agreement with the experimental data for approximately $t > 200$ s. We also indicate the time at which $\alpha_2^{(D)}(t)$ reaches a maximum, which lies close to this apparent onset of the long-time diffusive regime, seeming to indicate that we observe Fickian diffusion combined with non-Gaussian behaviour in agreement with previous reports.^{14,21} To probe this further, however, we consider the quantity $\delta r^2/4D_L t$ as a function of time, which we plot in the inset of Fig. 1c. In this representation, it is clear that the MSD is in fact only slowly approaching the hydrodynamic limit for times $t > 200$ s, and thus our observations do not imply a failure of the Gaussian approximation, but simply that it is difficult to infer from the MSD visually whether the true, asymptotic, long-time limit has been reached.

In order to consider both the time and lengthscale dependence of the non-Gaussian contributions to $F_s(k,t)$ and $G_s(x,t)$ in more detail we now attempt to determine directly the combinations of wavevectors and times at which the non-Gaussian behavior is seen. To this end, we consider the relaxation time scale $\tau_A(k)$ at which $F_s(k,t)$ decays to a given value A :

$$A = F_s(k, t = \tau_A(k)). \quad (9)$$

If $F_s(k,t)$ is Gaussian, then in the hydrodynamic limits for the colloidal system eqn (2) applies and eqn (9) becomes

$$A = \exp(-D_i k^2 \tau_A(k)), \quad (10)$$

where D_i with $i = S, L$ is the short- or long-time self-diffusion coefficient. From the definitions of the hydrodynamic limits, behaviour at large k and small t is expected to be governed by D_S , while that at small k and large t by D_L . It follows that

$$\frac{\ln A}{\tau_A(k)} = -D_i k^2, \quad (11)$$

such that a new function, $C(k)$, may be defined as

$$C(k) = \frac{\ln A}{\tau_A(k) k^2}. \quad (12)$$

For a fixed value of A , $C(k)$ approaches D_L for small values of k and D_S for large values of k . The intermediate k regime of $C(k)$ describes the crossover between the two diffusive regimes.

In Fig. 3 we show the variation of τ_A with k for A ranging from 0.9 to 0.1 for systems at $\phi = 0.08, 0.43$, and 0.62 . Here, results are considered in the form described by eqn (11) and thus the gradient is equal to $-D_i$. As such, lines corresponding to eqn (11) computed using the short- and long-time self-diffusion coefficients measured from the MSDs³⁴ are also shown. The comparison between the relaxation times of $F_s(k,t)$ and the two limiting gradients set by the self-diffusion coefficients in Fig. 3a–c clearly demonstrates

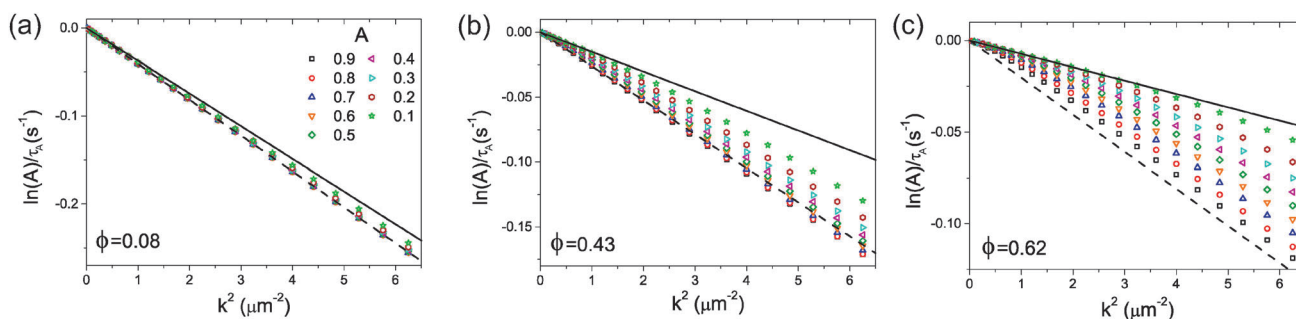


Fig. 3 The relaxation time as defined by eqn (11) as a function of k^2 shown for a range of values of A at (a) $\phi = 0.08$, (b) $\phi = 0.43$ and (c) $\phi = 0.62$. Values of A relate to all panels. Lines show the expected gradient from an independent measurement of the self-diffusion coefficients using the MSD. Here, the dashed line is calculated from the short-time self-diffusion coefficient, D_S , and the solid line from the long-time self-diffusion coefficient, D_L .



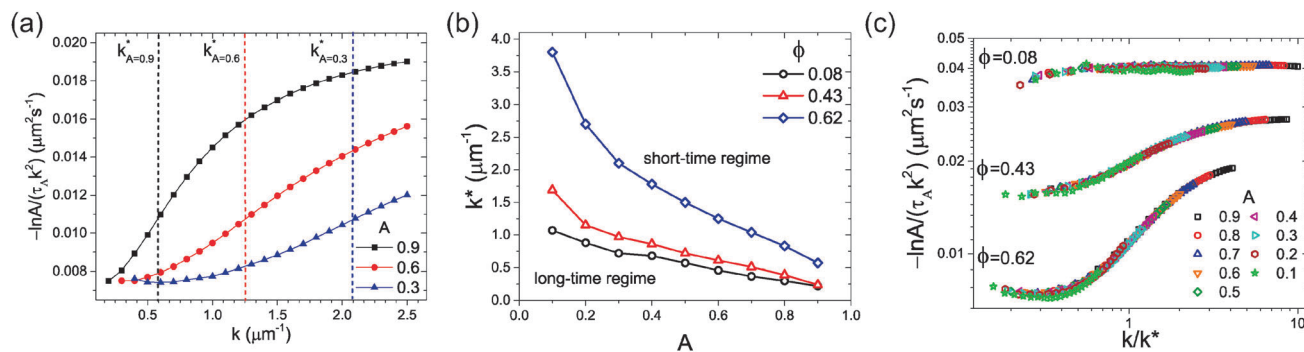


Fig. 4 (a) The dependence of the self-diffusion coefficient via eqn (11) on k for three different values of the parameter A at $\phi = 0.62$. Vertical dashed lines indicate the value of k^* for each curve. (b) The value of k^* as a function of A for systems at $\phi = 0.08, 0.43$ and 0.62 . (c) The variation of $C(k)$ (eqn (12)), with k rescaled by k^* for $\phi = 0.08, 0.43$ and 0.62 .

that there is a crossover from short to long-time behaviour with decreasing k and A . This is consistent with the fact that k is an inverse length scale and therefore relaxation times measured at higher k will reflect behaviour over shorter length scales which is naturally associated with shorter times. The value of A impacts upon the timescale probed; a longer time is required for $F_s(k, t)$ to decay to a lower value of A , and this automatically results in a consideration of behaviour at longer times.

The dependence of τ_A upon A is clearly much stronger for the systems at higher ϕ . This reflects the greater difference in the magnitude of the long- and short-time self-diffusion coefficients at higher ϕ .³⁴ Also evident is the difference in the timescales related to the short and long-time behaviour. For systems at low ϕ , a particle experiences relatively few direct interactions during a certain period of time due to the large average distance between particles. As such, the difference between the short-time and long-time diffusion coefficients, which arises from direct interactions, is relatively small, and only at very long times and length scales is the crossover to the long-time behaviour seen (see Fig. 3a). In contrast, for higher area fractions, the distance a particle must travel in order to directly interact with another particle is very short, resulting in significant number of direct interactions at short times. This both significantly reduces the value of the long-time self-diffusion coefficient relative to its short-time value, but also results in a crossover from the short- to long-time regime at much earlier time and smaller length scales. This is illustrated in Fig. 3c where $\ln A/\tau_A$ exhibits a gradient consistent with the long-time self-diffusion coefficient up to reasonably high values of k .

We now consider the trends displayed by Fig. 3 using the function $C(k)$ defined in eqn (12). In Fig. 4a we show the variation of $C(k)$ with k for three values of A for the system with $\phi = 0.62$. For each line it is possible to determine an inflection point at a certain value of k , which we denote as k^* , and these values are also indicated in Fig. 4a. The value of k^* indicates a crossover point between short- and long-time behaviour, and in Fig. 4b, k^* is plotted as a function of A . For all three values of ϕ , k^* increases with decreasing A . This arises from the fact that the behaviour at small A corresponds to that at long times and thus

long-time behaviour is seen even for large values of k . Furthermore, k^* for a fixed value of A is seen to increase with ϕ , demonstrating that as the area fraction increases, the length scale associated with the crossover between short- and long-time behaviour decreases. This is due to the fact that at lower ϕ the distance between particles is much greater and thus particles must diffuse further in order for sufficient collisions to occur to reach the long-time regime.

In Fig. 4c, $C(k)$ computed for all values of A is replotted with k now rescaled by k^* . This scaling relation is shown for systems with $\phi = 0.08, 0.43$, and 0.62 , where data for different values of A for each ϕ are seen to fall onto one master curve. Here, the presence of the long- and short-time regimes for the three different area fractions is clear, with the difference in long- and short-time behaviour seen to increase with ϕ . In addition to this, universal behaviour is seen with respect to the scaling relation at intermediate values of k close to k^* . This is surprising, due to the fact that the mechanisms that govern particle motion at intermediate lengthscales, and therefore times, are complex, and expected to differ with area fraction. Importantly, it is clear that both Fig. 3 and 4 provide significantly more information regarding the nature of the crossover from long- to short-time behaviour than that available from calculation of the non-Gaussian parameter. In particular, by determining the quantity k^* we are able to estimate the ranges of k for which the two hydrodynamic limits as a function of ϕ are seen.

5 Conclusions

We have computed the self-intermediate scattering function, $F_s(k, t)$, and the self-van Hove correlation function, $G_s(x, t)$, for a quasi-two-dimensional colloidal system, with a particular focus upon the estimation of these quantities using the Gaussian approximation. The Gaussian approximation is found to be in excellent agreement with a direct measurement of $G_s(x, t)$ and $F_s(k, t)$ for the full range of fluid area fractions in the relevant hydrodynamic regimes. This indicates that, in contrast to recent reports, the Gaussian approximation remains a useful tool in the discussion of particle dynamics providing that these



regimes can be identified. Furthermore, the fact that deviations from Gaussian behaviour disappear in the hydrodynamic regimes suggests that reports of Fickian yet non-Gaussian diffusion may arise from measurements outside the asymptotic long-time limit.

Small deviations from Gaussian behaviour are, however, found at intermediate times, and depend sensitively upon the area fraction and the wavevector at which the system is probed. These deviations are further quantified both through the non-Gaussian parameter, and more thoroughly *via* the relaxation times of $F_s(k, t)$. These relaxation times for systems at all area fractions are seen to obey a scaling relation, which allows the combinations of wavevectors and times at which the non-Gaussian behavior is seen to be determined. Furthermore, as this relation approaches the long-time self-diffusion coefficient for small values of k and short-time self-diffusion coefficient for large values of k it can be used to identify the two diffusive regimes and provides new insight into the crossover between them.

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