

## Experimental evidence for the divergence of a transport coefficient in a quasi-two-dimensional fluid

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(Received 1 August 1994)

We report experimental evidence for the divergence of the collective diffusion coefficient in a quasi-two-dimensional fluid. The system studied is a monolayer of nearly monodisperse self-assembled disks of the diblock copolymer polystyrene-*b*-polymethylmethacrylate, supported in the air/water interface, and the method used to measure the collective diffusion coefficient is dynamic evanescent wave light scattering. In all cases studied, in a system of interacting particles the collective diffusion coefficient, which depends on the sum of the time integrals of the velocity autocorrelation and crosscorrelation functions for all pairs of particles, is proportional to the self-diffusion coefficient. It has been predicted that the self-diffusion coefficient of a two-dimensional fluid does not exist, i.e., that the apparent self-diffusion coefficient defined by the time integral of the velocity autocorrelation function diverges as  $t \rightarrow \infty$ , implying that so, also, will the collective diffusion coefficient of a two-dimensional fluid. Our experimental data are consistent with this qualitative expectation and they also agree with the asymptotic dependence on time ( $t \rightarrow \infty$ ), wave vector ( $Q \rightarrow 0$ ), and surface density of the self-diffusion coefficient of a two-dimensional fluid predicted by Yuan and Oppenheim [H.H.-H. Yuan and I. Oppenheim, *Physica* **90A**, 1 (1978); **90A**, 21 (1978); **90A**, 561 (1978)].

PACS number(s): 61.20.-p, 51.10.+y

It has been known for about 20 years that the conventionally defined transport coefficients of a two-dimensional fluid diverge [1–5]. For example, the velocity autocorrelation function in a two-dimensional fluid is predicted to have the following asymptotic time dependence in the limit  $Q \rightarrow 0$  (with  $t$  measured relative to some fundamental relaxation time, e.g., the time between collisions in a gas) [6–8]:

$$\langle v(0)v(t) \rangle |_{Q \rightarrow 0} \sim (t\sqrt{\rho \ln t})^{-1}, \quad (1)$$

which implies that  $D \rightarrow \infty$  as  $t \rightarrow \infty$ . In addition, the self-diffusion coefficient is predicted to have the following dependence on wave vector in the limit  $Q \rightarrow 0$ ,

$$D(Q) |_{t \rightarrow \infty} \sim \sqrt{\rho^{-1} \ln(Q_c/Q)}, \quad (2)$$

which diverges as  $Q \rightarrow 0$ . In Eqs. (1) and (2)  $\rho$  is the density,  $Q$  is the wave vector of the density inhomogeneity, and  $Q_c$  is some cutoff wave vector. The asymptotic time dependence of the velocity autocorrelation function in a model two-dimensional colloidal suspension has been studied, via computer simulation, by van der Hoef, Frenkel, and Ladd [9], and shown to be consistent with the theoretical prediction. However, to date, there has not been an experimental verification of Eqs. (1) and (2).

Two issues which must be confronted immediately when experimental verifications of Eqs. (1) and (2) are sought are the following: (i) How does one generate a two-dimensional fluid for study? (ii) How can one measure the self-diffusion coefficient as a function of  $Q$  in the limit  $Q \rightarrow 0$ ?

In the three-dimensional world in which we live one

can only generate an approximation to a two-dimensional system by minimizing the unavoidable coupling of the system of interest to its surroundings. One case in which this effective decoupling has been demonstrated is a colloidal suspension in a very thin cell [10]. This paper reports the results of experimental studies of a very different system, namely, a quasi-two-dimensional fluid which consists of self-assembled disk shaped aggregates of a diblock copolymer, polystyrene-*b*-polymethylmethacrylate (PS-*b*-PMMA) ( $M_w$  880 000:290 000), supported at the air/water interface. We have previously shown that PS-*b*-PMMA diblock copolymers adsorbed at the air/water interface self-assembled into stable, nearly monodisperse, thin disks [11,12]. Each disk is composed of a dense core of the collapsed PS portions of the copolymers atop a thin layer of the PMMA portions of the copolymers on the water surface. At the periphery of each disk the PMMA components of the copolymers form a brush like boundary; the interaction between the disks is dominated by the effects associated with mixing the PMMA chains in the brush like boundaries. For the copolymer mentioned, the diameter of the dense core of the disk is about 2500 Å and the effective diameter of the full disk (including the brush boundary) is about 8000 Å.

The monolayer we study has a thickness of the order of a few tens of angstroms (the PMMA brush is about 18 Å thick and the PS disk core is no more than 70 Å thick) and linear dimensions in the interface of the order of tens of centimeters. The monolayer forms a distinct phase atop the supporting water, and is coupled hydrodynamically to the bulk fluid. The hydrodynamic behavior of a monolayer of interacting particles supported at the sur-

face of a bulk fluid has, to our knowledge, never been investigated either theoretically or experimentally. In this paper, we present the surprising result that said behavior closely resembles that expected for a true two-dimensional fluid [13].

The method we have used to study transport in the PS-*b*-PMMA monolayer is dynamic evanescent wave light scattering. The time dependence of the scattered light intensity autocorrelation function is related to relaxation phenomena with scale length equal to the inverse of the magnitude of the wave vector of the scattered light, specifically, for rigid particles, to relaxation associated with diffusion of the scattering centers over a distance equal to the scale length. For the wavelength and scattering angles used in the investigation reported in this paper that scale length ranges from less than the disk-disk separation to greater than the disk-disk separation. When  $Q$  is large relative to the inverse of the disk-disk separation we measure the self-diffusion coefficient. In contrast, in the limit  $Q \rightarrow 0$  the scale length probed becomes indefinitely large, hence the diffusion referred to is a collective response of the many particles in the domain spanned by the scale length; it is characterized by what has been called the collective diffusion coefficient. The collective diffusion coefficient can be represented as a sum of the time integrals of the velocity autocorrelation and cross correlation functions for all pairs of particles [14]. Because of the interactions between the particles, the self-diffusion coefficient and the collective diffusion coefficient are different except in the limit of infinite dilution. For those cases that have been studied, all of which are three-dimensional model systems, the collective diffusion coefficient can be represented as the product of the self-diffusion coefficient and a concentration dependent function that reflects the effects of particle-particle interaction, both potential and hydrodynamic. If that factorization remains valid for a two-dimensional fluid, the predicted asymptotic dependence of the self-diffusion coefficient on  $t$  and  $Q$  should generate the same dependences in the collective diffusion coefficient. In the experiments reported in this paper we have measured both the self- and collective diffusion coefficients for particular ranges of  $Q$ . Our results show that the collective diffusion coefficient of the disks in the monolayer of PS-*b*-PMMA exhibits the divergences as  $t \rightarrow \infty$  and  $Q \rightarrow 0$  that are predicted to occur in the self-diffusion coefficient of a two-dimensional fluid.

The principle underlying the evanescent wave light scattering method and the apparatus used to measure said scattering have been described elsewhere [12]. The self-assembled disks of (PS-*b*-PMMA), prepared at the air/water interface in a Langmuir trough, are illuminated with an Ar ion laser,  $\lambda = 5145 \text{ \AA}$ , in a manner which generates a surface-confined evanescent field on the air side of the interface. In the studies of the static structure factor we used a multiplexed detector with a coherent fiber bundle; the 71 fibers, which are distributed from  $\sim 0^\circ$ – $180^\circ$ , carry the scattered light to an optical multichannel analyzer. In the studies of the dynamic light scattering, a single optical fiber was used to collect the scattered light and carry it to a photomultiplier tube.

The temporal intensity autocorrelation function is obtained using a digital correlator (BIAT9000). The angular range covered in the dynamic light scattering measurements reported in this paper is  $\sim 0^\circ$ – $35^\circ$ , and  $55^\circ$ – $125^\circ$ , with a pickoff angle (out-of-plane) of approximately  $20^\circ$ . The range of the in-plane scattering vector  $Q_{xy}$  is from  $9.6 \times 10^3 \text{ cm}^{-1}$  to  $2.6 \times 10^5 \text{ cm}^{-1}$ . For simplicity, since our studies do not concern the out-of-plane component of the scattering vector we denote the in plane scattering vector  $Q$ .

The samples studied were prepared in the same fashion as reported earlier [12]; the data reported in this paper were taken at  $T = 18^\circ \text{C}$ . A very dilute solution ( $\sim 0.03 \text{ mg/mL}$  in chloroform) of PS-*b*-PMMA was spread onto the surface of water dropwise in a virtually dust free Langmuir trough. The polymer monolayer was left on the surface of the water for about eight hours and then was subjected to a compression/expansion/recompression "annealing" cycle. After compressing the polymer monolayer to a particular surface coverage, and before the light scattering measurements were carried out,  $\sim 0.5 \text{ mL}$  of pure chloroform was spread over the film. We display in Fig. 1 the isotherms of a PS-*b*-PMMA monolayer before and after the spreading of chloroform; these data show that spreading the solvent over the monolayer reduces the average minimum area occupied by a monomer at the surface, which implies that the application of the solvent improved the homogeneity of the monolayer. This implication is confirmed by the results reported below. In contrast, it has been shown [12,15] that the conventional preparation of a monolayer of PS-*b*-PMMA at the air/water interface, i.e., compressing the monolayer only once, produces large rafts of aggregates of the polymer and a rather polydisperse distribution of disks.

The structure factors extracted from the static light scattering data, for the entire range of surface coverage studied, namely, from one monomer/ $18 \text{ \AA}^2$  to one monomer/ $2.5 \text{ \AA}^2$ , and fits to those data using the structure factor of the hard disk fluid [16], are displayed in Fig. 2.

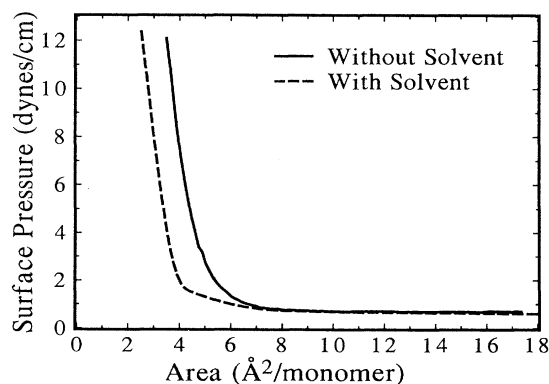


FIG. 1. Surface pressure-surface coverage isotherms for an adsorbed PS-*b*-PMMA (880:290 K) monolayer at the air/water interface ( $T = 18^\circ \text{C}$ ); —: isotherm taken before pure solvent was spread over the monolayer, and - - -: isotherm taken after pure solvent was spread over the monolayer (see text).

These fits were made with the assumption that the self-assembled disks are monodisperse. Clearly, as the surface coverage increases the width of the peak in the structure factor decreases and its height increases. There have been several theoretical studies of the influence of polydispersity on the structure factor of an assembly of spheres [17]. The results of those studies, coupled with the success of our fits to the data, strongly support the assumption that the monolayers we have studied are composed of nearly monodisperse disks.

As shown in our earlier work [12], the distribution of PMMA chains in the brushlike boundary of a disk does not contribute substantially to the observed intensity of scattered light, presumably because that brush boundary has only a small difference in refractive index from that of the substrate water. Thus, the fits of the static structure factor described above use the diameter of the dense PS core of the disk. At a surface density of one monomer/ $6 \text{ \AA}^2$  the packing density of the PS cores, treated as hard disks, is 0.34, and the brushlike boundaries form a concentrated mixture of chains; at this and smaller packing densities the system of self-assembled polymer aggregates appears to be fluid. At higher surface densities the interactions between the chains in the brushlike bound-

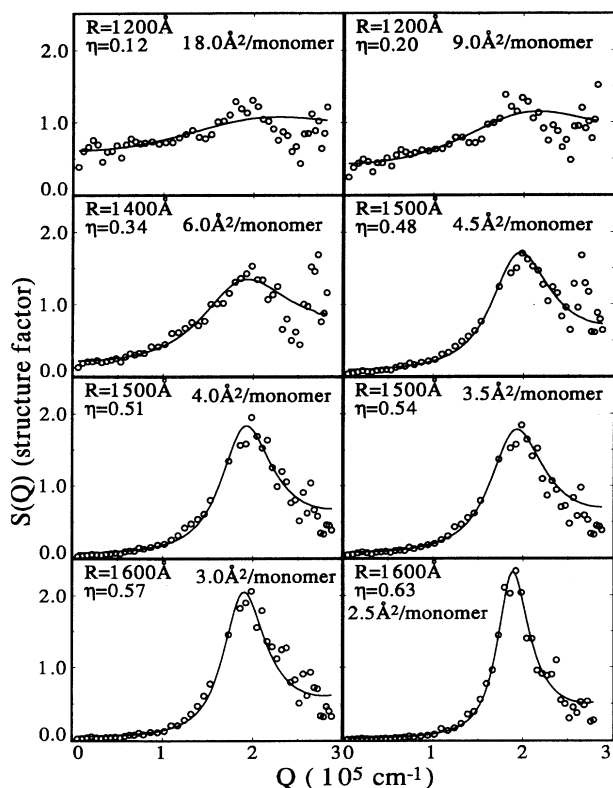


FIG. 2. The static structure factors for the adsorbed PS-*b*-PMMA (880:290 K) monolayer at the air/water interface for the surface coverage range one monomer/ $18 \text{ \AA}^2$  to one monomer/ $2.5 \text{ \AA}^2$ . The solid lines are fits to the data to the theoretical structure factor of a two-dimensional hard disk fluid;  $R$  and  $\eta$  are the fitted hard disk radius and packing fraction of the disks, respectively.

aries of the disks becomes sufficiently strong that motion of the assembly of aggregates become very sluggish, possibly nonergodic on the time and length scales of the light scattering experiment. We interpret the adequacy of the fits of the static structure factor in this surface concentration range to indicate continuity of states from the domain of equilibrium states into the domain of non-equilibrium states. In this sense, these fits are analogous to the fitting, in three dimensions, of the structure factor of a glass to that of an "effective fluid." Note, however, aside from a larger than expected drop in the effective diffusion coefficient for surface densities greater than one monomer/ $6 \text{ \AA}^2$  we have no evidence for the formation of a two-dimensional glass in our system.

The temporal autocorrelation function of the scattered light intensity,  $g^{(1)}(t, Q)$ , was obtained for eight different surface coverages ranging from one monomer/ $18 \text{ \AA}^2$  to one monomer/ $3.0 \text{ \AA}^2$ ; the corresponding hard disk packing fractions are  $\eta \sim 0.12$  to 0.57. At each surface coverage the intensity autocorrelation function was measured at 25 values of the scattering vector  $Q$  from  $9.6 \times 10^3 \text{ cm}^{-1}$  to  $2.6 \times 10^5 \text{ cm}^{-1}$ . The display time for a typical intensity autocorrelation function is approximately 1 sec and the duration of a scan is 15 min.

Our results can be viewed at two levels of interpretation. First, do the experimental data yield evidence for the predicted divergence of the collective diffusion constant? We shall show that the answer to this question is yes. Second, does the form of the divergence of the collective diffusion coefficient follow the predicted asymptotic behavior? We shall show that the answer to this question is also yes.

The key step in our analysis is the identification of the ranges of time, wave vector, and surface density for which the measured collective diffusion coefficient is expected to display asymptotic behavior. To examine the time dependence of the self-diffusion coefficient we restrict attention to the wave vector range corresponding to distances smaller than the average disk-disk separation ( $Q > Q_m = 1.9 \times 10^5 \text{ cm}^{-1}$ , the value at the peak of the static structure factor) and to a time interval short enough that a disk can diffuse only a small fraction of the average disk-disk separation. To study the functional form of the collective diffusion coefficient as  $Q \rightarrow 0$  we restrict attention to the range  $Q < Q_m$ . In both analyses we must also restrict attention to the surface concentration domain in which the self-assembled polymer aggregates behave as a fluid assembly of disks.

As mentioned earlier, the time in Eq. (1) is measured relative to a characteristic relaxation time for the system. For our system one such characteristic time is that associated with the propagation of a viscous shear wave a distance equal to the distance between disks [18], which is  $\tau_H = \rho \Lambda^2 / \eta_0$ , where  $\rho$  is the density of the liquid,  $\Lambda$  the average disk-disk separation, and  $\eta_0$  the viscosity of the liquid. If we restrict the time scale such that the hydrodynamic perturbation cannot propagate further than, say,  $\Lambda/10$ , we find, for the conditions of our experiment,  $\tau_H \approx 2 \times 10^{-9} \text{ s}$ . Another such characteristic time is that associated with the fluctuations induced by collisions between the supporting liquid and a disk, which is

$\tau_B \approx M/3\pi\eta_0R$ , where  $M$  is the mass of a disk with radius  $R$ . For our system  $\tau_B \approx 2 \times 10^{-10}$  s. The overall time interval we consider is of order  $100 \mu\text{s}$ , and the sampling interval we consider is  $10 \mu\text{s}$ , both of which are sufficiently greater than these characteristic times that we expect to be in the asymptotic time domain even in the initial stage of the decay of the temporal intensity autocorrelation function. The characteristic length scale associated with the development of a hydrodynamic interaction by which the supporting liquid influences the motion of the disk is  $L_H^2 = \eta_0/\nu\xi$ , where  $\nu$  is the monomer density of the PMMA brush in the peripheral region of the disk and  $\xi$  is the friction coefficient of a PMMA monomer;  $L_H$  is about  $10 \text{ \AA}$  for our system [12]. This characteristic length is much smaller than the average disk-disk separation, hence corresponds to wave vectors greater than that characteristic of the first peak of the static structure function. Indeed, over the entire range of  $Q$  that we have studied, the magnitude of the wave vector is very small relative to the inverse of the hydrodynamic shielding length.

To show that our data display the qualitative features of the predicted divergence of the collective diffusion coefficient we first examine its behavior in  $Q$  space. The temporal intensity autocorrelation function can be fitted to the first term of a cumulant expansion [19],

$$\ln g^{(1)}(t) = \lim_{t \rightarrow 0} [-K_1(Q)t], \quad (3)$$

in which a typical cutoff time is a few milliseconds. The first cumulant  $K_1(Q)$  defines an effective diffusion coefficient [18],  $D_{\text{eff}}(Q)$ , governing the decay of  $g^{(1)}(t)$ :

$$D_{\text{eff}}(Q) = \frac{K_1(Q)}{Q^2} = \frac{D_0H(Q)}{S(Q)}, \quad (4)$$

where

$$D_0H(Q) = \frac{1}{3N} \sum_i \sum_j \int_0^\infty \langle V_i(0)V_j(t) \rangle dt. \quad (4')$$

In Eq. (4')  $S(Q)$  is the static structure factor,  $D_0$  the free particle diffusion coefficient, and  $H(Q)$  a factor describing the effects of hydrodynamic interactions. It is important to note that in conventional hydrodynamic theory

the diffusion coefficient is defined as in Eq. (4'), instead of Eq. (4); the latter is generally used in dynamic light scattering measurements. Thus, we compare the behavior of  $D_0H(Q)$  instead of  $D_{\text{eff}}$  with Eq. (2). When  $Q$  is small  $D_0H(Q)$  is the collective diffusion coefficient; when  $Q$  is large  $D_0H(Q)$  is the self-diffusion coefficient [ $H(Q) \sim 1$  when  $Q$  is large]. We show in Fig. 3 a typical plot of  $D_0H(Q)$  versus  $Q$ ; the apparent divergence of  $D_0H(Q)$  as  $Q \rightarrow 0$  is clearly seen at this surface coverage and for all the other surface coverages studied.

We now examine the behavior of the self-diffusion coefficient as a function of time. To do so we consider the mean square displacement,  $\langle \Delta x^2(t) \rangle$ , which has the asymptotic ( $t \rightarrow \infty$ ) time dependence [6]

$$\langle \Delta x^2(t) \rangle \sim \frac{t\sqrt{\ln t}}{\sqrt{\rho}}, \quad (5)$$

and which can be determined from [18]

$$g^{(1)}(t) = \exp \left[ -\frac{Q^2}{4} \langle \Delta x^2(t) \rangle \right], \quad (6)$$

where the decay of the correlation function can be interpreted in terms of the mean square displacement of an individual particle, provided that  $Q > Q_m$ . We show in Fig. 4, for a particular value of the wave vector ( $Q = 2.6 \times 10^5 \text{ cm}^{-1}$ ), that  $\langle \Delta x^2(t) \rangle/t$  increases as  $t$  increases, as predicted in Eq. (5). Recall that the collective diffusion coefficient is proportional to the self-diffusion coefficient, so the same asymptotic dependence on time is expected.

We draw the strong conclusion that the qualitative features of the predicted divergence of the collective diffusion coefficient in a two-dimensional fluid, as  $t \rightarrow \infty$  and as  $Q \rightarrow 0$ , are verified by our experimental data.

To test the predicted functional form of the asymptotic dependence on  $Q$  we show in Fig. 5 the collective diffusion coefficient as a function of  $[\ln(Q_m/Q)]^{1/2}$ . The solid lines in Fig. 5 are the fits of the collective diffusion coefficients to Eq. (2); in this range of  $Q$  ( $\sim 9.6 \times 10^3 \text{ cm}^{-1}$  to  $4.0 \times 10^4 \text{ cm}^{-1}$ ) our data agree, within our experimental precision, with the theory. We have also verified the dependence of the collective diffusion coefficient on the particle density predicted by Eq. (2).

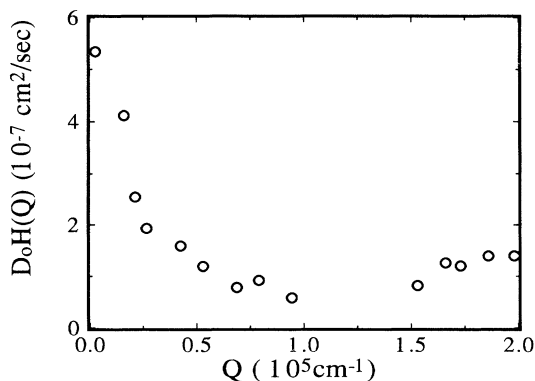


FIG. 3. Typical behavior of the collective diffusion coefficient  $D_c(Q)$  of the adsorbed PS-*b*-PMMA (880:290 K) monolayer in the limit of small wave vector  $Q$ ; the surface coverage is one monomer/ $18 \text{ \AA}^2$  for this particular set of data.

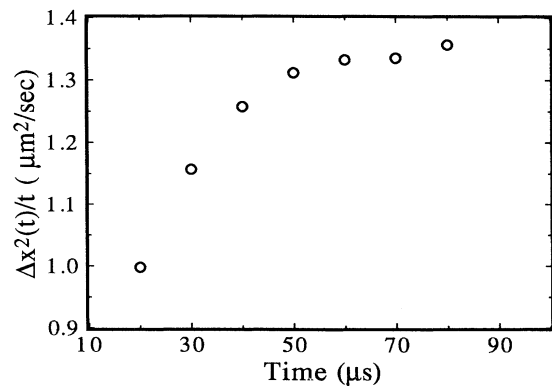


FIG. 4. Typical behavior of the mean square displacement,  $\langle \Delta x^2(t) \rangle$ , divided by time  $t$  at  $Q = 2.6 \times 10^5 \text{ cm}^{-1}$ , in the long time limit; the surface coverage is one monomer/ $18 \text{ \AA}^2$  for this particular set of data.

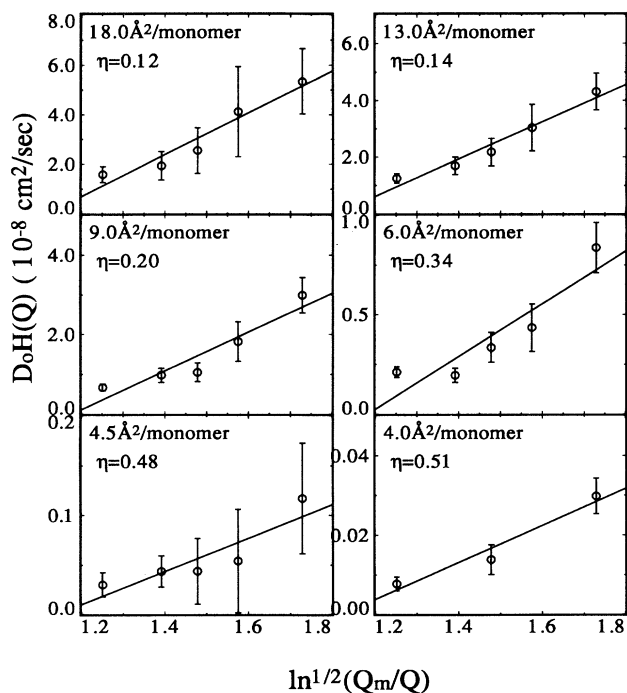


FIG. 5. The collective diffusion coefficient as a function of  $[\ln(Q_m/Q)]^{1/2}$  for the packing fraction range from  $\sim 0.12$  to  $0.51$ ; the solid lines are the fits of  $D_c(Q)$  to Eq. (2). In the plots  $Q$  extends from  $9.6 \times 10^3 \text{ cm}^{-1}$  to  $4.0 \times 10^4 \text{ cm}^{-1}$  and  $Q_m$  is the position of the first peak in the static structure factor (see Fig. 2).

Figure 6 shows a linear fit of the slopes from Fig. 5 to the inverse square root of the packing fraction  $\eta$  for the region of  $\eta \sim 0.12$ – $0.34$  in which we are confident that the system is fluid; the agreement between the inferred and observed density dependence of the collective diffusion coefficient is reasonably good.

Figure 7 shows the mean square displacement divided by  $t$  at  $Q = 2.6 \times 10^5 \text{ cm}^{-1}$  as a function of  $[\ln(t/t_s)]^{1/2}$  for the packing fraction range from  $0.12$  to  $0.51$  and for the time domain of  $20 \mu\text{s} < t < 80 \mu\text{s}$ ; the sampling time  $t_s$  is  $10 \mu\text{s}$ . Clearly, up to  $34\%$  of surface coverage, the data agree very well with the theory. (See also Fig. 8.)

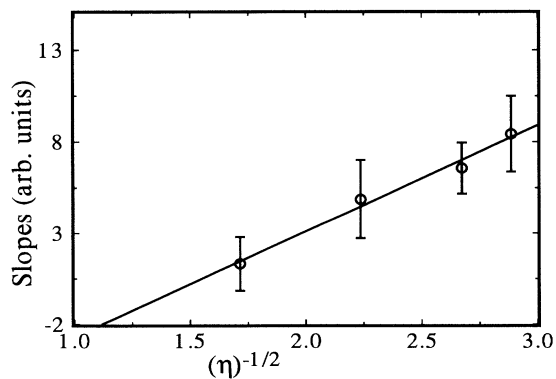


FIG. 6. A linear fit of the slopes from Fig. 5 to  $\eta^{-1/2}$  for the region  $\eta \sim 0.12$ – $0.34$ .

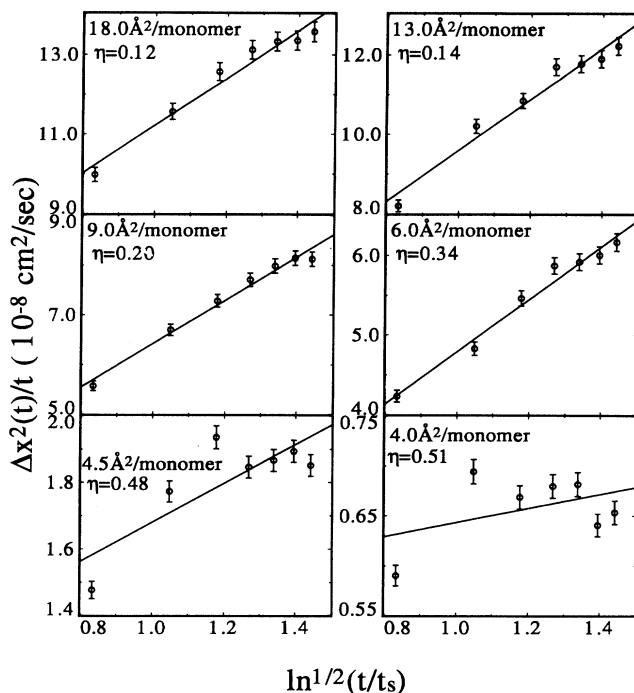


FIG. 7. The mean square displacement,  $\langle \Delta x^2(x) \rangle$ , divided by time  $t$  at  $Q = 2.6 \times 10^5 \text{ cm}^{-1}$  as a function of  $[\ln(t/t_s)]^{1/2}$  for the packing fraction range  $\sim 0.12$ – $0.51$ ; the solid lines are the fits of  $\langle \Delta x^2(t) \rangle / t$  to Eq. (1).

We conclude that, within our experimental precision, the functional forms of the asymptotic dependence of the collective diffusion coefficient of a two-dimensional fluid on  $t$  and  $Q$  are correctly given by Eqs. (1) and (2).

The model we have used to analyze our data is the analog of the widely accepted model of colloid solutions, i.e., we assume that the role of the solvent can be subsumed into an effective interaction between the particles, so that it is possible to represent the system as a pseudo one component fluid. This model introduces no complications unless the particle property studied has a divergence as the density goes to zero. Thus, the model can accurately

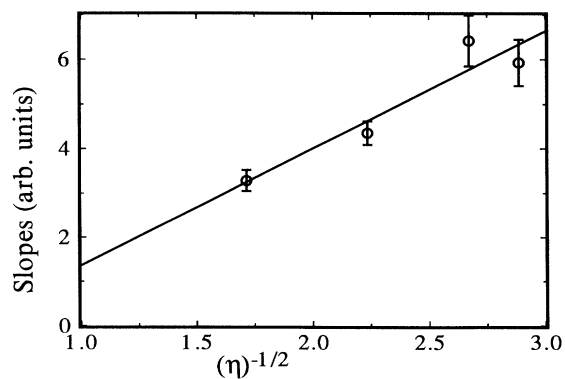


FIG. 8. A linear fit of the slopes from Fig. 7 to  $\eta^{-1/2}$  for the region  $\eta \sim 0.12$ – $0.34$ .

represent the static structure function of the two-dimensional assembly of disks for all surface densities for which that assembly is fluid. However, the diffusion coefficient of a one component two-dimensional fluid diverges in the limit as the density goes to zero because the mean free path becomes indefinitely large, whereas the diffusion coefficient of our assembly of disks remains finite as the surface concentration goes to zero because the friction between a disk and the supporting water does not vanish in the limit of infinite dilution. Accordingly, our test of the density dependence of the asymptotic form of the collective diffusion coefficient can only be valid for surface concentrations greater than some threshold value. The lowest surface concentration we have studied, with a packing fraction of 0.12, is sufficiently large to be out of the "dilute gas" range, so we believe that our analysis of the density dependence of the apparent diffusion coefficient is appropriate.

Our data set covers a larger range of time, wave vector and surface concentration than we have used in the asymptotic analysis just described. As already noted, the restriction of our analysis to surface concentrations equal to or less than one monomer/ $6 \text{ \AA}^2$  is necessary to guarantee that the observed time dependent light scattering is generated by fluid states of the system, whereas the restrictions of the analysis to the ranges of  $t$  and  $Q$  considered are intended to define the asymptotic domains of the dependence of the collective or self-diffusion coefficients on those variables.

For values of  $t$  and  $Q$  outside what we consider to be the asymptotic range the behavior of the effective diffusion coefficient is rather different from that in the asymptotic range. For example, for  $Q > 4 \times 10^4 \text{ cm}^{-1}$  our data start to deviate from the functional form displayed in Eq. (2). Similarly, for  $t > 80 \text{ \mu s}$  our data start to depart from the functional form displayed in Eq. (1). In this near asymptotic region the assumption that  $Q$  is small relative to the hydrodynamic length scale defined by flow of the solvent around the disk, and that  $t$  is large relative to the fundamental hydrodynamic relaxation time, remain valid. We believe that the behavior observed arises from the internal structure of the self-assembled polymer disks, i.e., that other relaxation processes, associated with intradisk motions, start to contribute to the effective diffusion coefficient. Our data show that, overall, the inverse of the effective diffusion coefficient as a function of  $Q$  broadly resembles the static structure function, but that the position of the peak in  $D_{\text{eff}}(Q)^{-1}$  deviates significantly from that of the peak in  $S(Q)$ , and the shapes of the peaks are not identical [17]. A quantitative analysis of these data must await development of the

theory of the effective diffusion coefficient of particles with internal degrees of freedom.

The observed agreement between our experimental results and the theoretical predicted hydrodynamic behavior for a two-dimensional fluid is striking; both the  $Q$  dependence and the  $t$  dependence exhibit the divergences expected, and the density dependence exhibits the predicted  $\eta^{1/2}$  behavior. The highly unusual functional form of these divergences, the square root of a logarithm, is compelling evidence in support of this interpretation. This observation is remarkable since the system we have studied is not a true two-dimensional fluid; nevertheless, the experimental results strongly imply that it behaves hydrodynamically in the fashion predicted for a two-dimensional fluid. It is conceivable that some other effects could be responsible for the observed behavior; however, none of the most likely possibilities are consistent with our observations. For example, polydispersity of the disk radii could distort the interpretation of the dynamic light scattering data. However, the quality of the fit of the static structure function to that for a fluid of monodisperse hard disks strongly suggests that the distribution of disk radii is narrow. In particular, polydispersity leads to a substantial increase the scattered light intensity as  $Q \rightarrow 0$  [14], and our data do not exhibit this behavior. Alternatively, some unsuspected long-ranged interaction between the polymer brushes at the peripheries of the disks might lead to anomalous behavior as  $Q \rightarrow 0$ . However, as shown in Figs. 3 and 5, the observed divergence of  $D_c$  persists down to rather low surface densities where such an interaction ought to generate at most a very weak perturbation to the system properties. And, our interpretation of the surface pressure-surface area isotherm does not invoke any long range interaction, only the effects arising from mixing of the chains attached to the peripheries of the disks. Thus, we conclude that the most likely explanation of the observed behavior is that the monolayer behaves very much like a true two-dimensional fluid. Theoretical calculations, or computer simulations, of a fluid of disks supported on the surface of a liquid are clearly required to further explore this fascinating analogy.

We thank Professor Irwin Oppenheim for a valuable discussion of the character of the asymptotic representation of transport coefficients in a two-dimensional fluid. This research was supported by a grant from the National Science Foundation (NSF CHE-9220590). We have also benefited from facilities provided by the NSF for materials research at The University of Chicago (NSF DMR-8819860).

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