Anomalous Diffusion at Liquid Surfaces

Oleg V. Bychuk[1] and Ben O'Shaughnessy[2]

[1]*Department of Physics, Columbia University, New York, New York 10027*
[2]*Department of Chemical Engineering, Materials Science and Mining Engineering, Columbia University,*
New York, New York 10027

We study the role of bulk-surface exchange in the diffusion of adsorbed molecules at liquid-solid and liquid-fluid interfaces. For "strong adsorbers" (readsorption time much less than desorption time) we find anomalous surface diffusion on time scales less than the surface retention time: Displacement moments grow as $\langle r^q \rangle \sim t^{\zeta(q)}$, where $\zeta(q) = q$ for $q < 1$, $\zeta(q) = (q + 1)/2$ for $q > 1$, and $\langle r \rangle \sim t \ln t$. This superdiffusive behavior arises because molecules execute Lévy walks on the surface, mediated by the liquid bulk.

The dynamics of adsorbed molecules are a fundamental issue in interface science [1–10] and are crucial to a number of emerging technologies [3,11]. Their role is central to phenomena as diverse as foam relaxation [12] and the evolution of blood protein deposits [13]. Experimental studies of surfactant molecules [5–7], proteins [9,10,14], and synthetic polymers [8,10] confined to interfaces have identified two types of surface translational motions. One is in-surface self-diffusion of individual molecules, which has been investigated with fluorescence recovery after photobleaching (FRAP) methods [4,10,14]. Measured self-diffusivities at liquid-solid interfaces are much smaller than bulk values [14], and similar to bulk values in liquid-gas cases [10]. A second source of motion, exclusive to the liquid-fluid interface, is surface viscoelasticity: Adsorbed surface phases possess compressibility and viscosities which govern the dynamics of surface density waves. Their relaxation kinetics have been intensively researched experimentally [5–7] and theoretically [1,2,15,16]; direct viscoelastic measurements [5] and surface light scattering studies [4,15,16] provide considerable support for current theories.

In this Letter we identify and explore a third mechanism: bulk-mediated effective surface diffusion. This mechanism arises at interfaces separating a liquid bulk phase and a second phase which may be either solid, liquid, or gaseous. Whenever the adsorbed species are soluble in the liquid bulk, adsorption-desorption processes occur continuously. These generate surface displacement because molecules desorb, undergo Fickian diffusion in the bulk liquid, and then readsorb elsewhere (see Fig. 1). Repeated many times, this results in effective diffusion of a molecule on the surface. The importance of bulk-surface exchange in relaxing *homogeneous* surface density perturbations is well established experimentally [1,2,5–9,17]. Our aim here is to establish their role in relaxing *inhomogeneous* density perturbations and the nature of the molecular self-diffusion which they generate.

The discussion which follows will be quite general. We consider an interface separating a bulk liquid, into which adsorbate molecules make excursions, from a second phase which is arbitrary. When the bulk-mediated mechanism dominates (competing mechanisms are discussed later) we will see that this leads to a non-Fickian surface diffusion law and "anomalous scaling," i.e., a nontrivial family of scaling exponents governing the moments of particle displacement. In the present case these peculiar statistics arise because individual molecules perform "Lévy walks" [18,19] on the surface. The unusual statistics of Lévy processes have been invoked to explain a number of physical phenomena such as transport in disordered solids [20] and self-diffusion in wormlike micelle systems [21]. Our study has resulted in a range of experimental predictions whose validity is strongly corroborated by computer experiment.

At first sight, it may seem odd that the displacement statistics of molecules due to this bulk-mediated mechanism should be so unusual. Molecules perform random walks on the surface, each step consisting of a single bulk excursion followed by a waiting period before the next desorption. It is thus natural to anticipate "standard" random walk statistics, i.e., the familiar diffusion result with surface displacement r scaling with time t according to Fick's law, $r \sim t^{1/2}$. The origin of Fick's law lies in the central limit theorem [22], according to which the sum of many independent variables follows a Gaussian distribution, provided each variable has finite second moment.
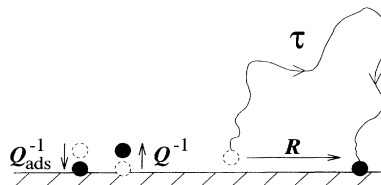

FIG. 1. Adsorption-desorption kinetics of bulk-soluble surfactants. A molecule within b of the interface adsorbs with probability Q_{ads} per unit time. An adsorbed molecule desorbs after time Q^{-1}, then executing an excursion into the liquid bulk lasting τ before readsorption. The excursion results in surface displacement **R**. Bulk-mediated effective surface diffusion results from a sequence of bulk excursions.

This implies $r \sim n^{1/2}$, after n independent random walk steps. Now, provided the first moment of the time elapsed during one step is finite, it follows also that $t \sim n$. These two relations lead to the Fickian result.

The key point is that these familiar relations are actually *not* applicable to the bulk-mediated mechanism. We consider a dilute surfactant-containing liquid bulk confronting a planar interface which adsorbs molecules within a distance b at a rate Q_{ads} (see Fig. 1). Consider a molecule which has just desorbed from the interface. It is straightforward to show that after many collisions with the surface it inevitably gets readsorbed after a "typical" time $t^* = D/(Q_{ads}b)^2$, where D is its bulk diffusivity. However, this is an oversimplification. We have exactly calculated the distributions $\psi(\tau)$ and $\phi(\mathbf{R})$ of readsorption times τ and displacements $\mathbf{R}$ (see Fig. 1) during one such bulk excursion, finding that they in fact possess *long algebraic tails:*

$$\psi(\tau) \approx t^{*-1}(t^*/\tau)^{3/2} \quad (\tau > t^*),$$
$$\phi(\mathbf{R}) \approx r^{*-2}(r^*/R)^3 \quad (R > r^*), \tag{1}$$

where $r^* \equiv (Dt^*)^{1/2}$ is the diffusion length corresponding to t^*. These forms can be understood in terms of the long time behavior of the "survival probability" $S(\tau) \sim \tau^{-1/2}$, namely, the probability a random walker initially a distance r^* from the interface has never touched it by the time τ. Equation (1) then follows from $\psi \approx -dS/d\tau$ and $R \approx (D\tau)^{1/2}$. Thus, both the second moment of displacement and the first moment of time elapsed during one step are infinite. A random process of this type is known as a Lévy walk [18,19]: The central limit theorem breaks down and Fick's law is inapplicable.

We will now show that the long tails of the one-step distributions in Eq. (1), combined with the waiting periods between bulk excursions, lead to an anomalous "superdiffusive" surface displacement, $r \sim t$. Let us begin by estimating the total time spent in the bulk after n bulk excursions, t^{bulk}. Since roughly $n\psi(\tau)d\tau$ steps lasted between τ and $\tau + d\tau$, and since the contribution from scales less than t^* can be shown to be small, one has $\int_{t^*}^{t^{bulk}} \tau[n\psi(\tau)d\tau] \approx t^{bulk}$, whence $t^{bulk} \approx n^2t^*$. But r and t^{bulk} are related in the standard manner, $r \approx (Dt^{bulk})^{1/2}$, since molecular displacement arises through simple diffusion in the bulk. Hence it immediately follows that $r \approx nr^*$. These two results are very different to the usual scalings, $t^{bulk} \approx nt^*$ and $r \approx n^{1/2}r^*$, which would pertain for well-behaved distributions.

We want the dependence of r on the *total* time elapsed t. It is important to realize that between bulk excursions a molecule spends a certain amount of time in the adsorbed state on the surface. Assuming a well-behaved distribution of desorption times with characteristic scale Q^{-1}, the total time spent on the surface after n excursions is simply $t^{surf} \approx nQ^{-1}$. The key quantities thus read

$$t^{bulk} \approx n^2t^*, \quad t^{surf} \approx nQ^{-1}, \quad r \approx nr^*. \tag{2}$$

Now for small n, $n \ll 1/Qt^*$, Eq. (2) tells us that the time spent on the surface is much greater than that in the bulk,

i.e., $t = t^{surf} + t^{bulk} \approx t^{surf}$. Thus

$$t \approx nQ^{-1} \quad (t \ll t_h), \tag{3}$$

where $n \ll 1/Qt^*$ was restated in terms of the important time scale $t_h \equiv 1/Q^2t^*$.

Before proceeding, it is crucial to note that the arguments leading to Eq. (3) make sense only for bulk-interface systems for which $Q^{-1} \gg t^*$. We refer to such systems as "strong adsorbers." In strong systems, for times $t \ll t_h$ a molecule spends almost all of its time on the surface during a sequence of desorption-readsorption events, while for $t \gg t_h$ its time in the bulk is much greater. Hence t_h is identified as the *surface retention time*. The definition of a strong system can be restated as $t_h \gg Q^{-1}$; the retention time greatly exceeds the desorption time. Molecules are desorbing and readsorbing, and yet are not being permanently lost to the bulk; instead, they are moving from one surface location to another. This is the anomalous effective surface diffusion referred to above, which persists until the surface loses its occupants after t_h. It results in a surface displacement which [$h \equiv (Dt_h)^{1/2}$] from Eqs. (2) and (3) grows *linearly* in time with a "speed" c,

$$r \approx ct, \quad c = D/h \quad (t \ll t_h). \tag{4}$$

We remark that this anomalous surface diffusion is related to another characteristic feature of strong systems: It can be shown that they exhibit diffusion control in the bulk liquid, resulting in algebraic relaxation of *homogeneous* surface density perturbations [1], $\delta\Gamma(t)/\delta\Gamma(0) \approx 1 - \text{const} \times (t/t_h)^{1/2}$. The relaxation time is t_h, and h turns out to be the slope of the equilibrium coverage isotherm $h \equiv \partial\Gamma/\partial p$, where Γ and p denote surface and bulk concentrations, respectively. "Weak" systems, $Qt^* \gg 1$, behave very differently: There is no bulk-mediated diffusion and molecules are released after a single desorption time, $\delta\Gamma \sim e^{-Qt}$.

We have confirmed these simplified arguments leading to $r \approx ct$ by rigorous analysis of the Lévy walk performed by each molecule on the surface. Instead of the familiar Gaussian, we find the distribution of possible particle displacements has a long $1/r^3$ tail:

$$P(\mathbf{r}, t) = (ct/2\pi)[(ct)^2 + r^2]^{-3/2}, \quad r \ll (Dt)^{1/2}. \tag{5}$$

This is a "Cauchy" distribution [19] of width ct. We have tested these analytical predictions by extensive numerical simulations. A particle initially adsorbed on a planar surface desorbs with probability Q per time step. If desorbed, it random walks on a cubic lattice, making one lattice hop per time step and readsorbing with probability Q_{ads} per time step should it reach a site adjacent to the surface. The results of Fig. 2(a) are in excellent agreement with the $r \sim t$ scaling prediction, for displacement moments $\langle r^q(t) \rangle$, with $q = 0.2$ and $q = 0.5$, after an initial ($Qt \lesssim 10$) transient regime. The moments were obtained by averaging over $N = 6 \times 10^4$ independent particle walks, each walk consisting
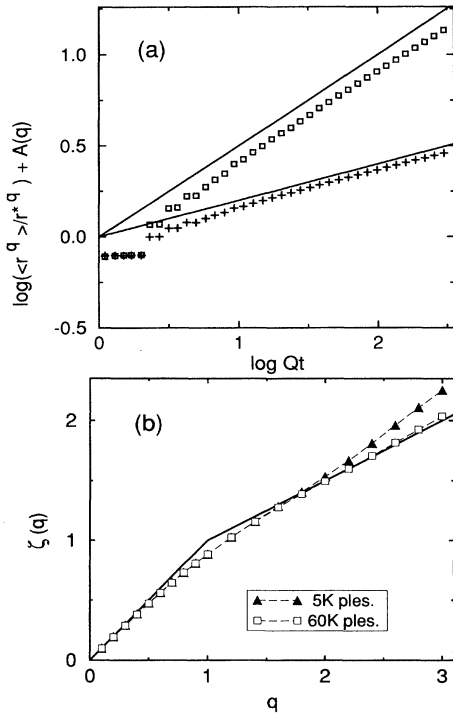
FIG. 2. Numerical results for a strongly absorbing system ($Qt_h = 6 \times 10^5, Q^{-1} = 10^7$ time steps). (a) Log-log plots of dimensionless qth moment of displacement r, averaged over 6×10^4 particle walks, versus dimensionless time for $q = 0.2$ (+) and $q = 0.5$ ($\square$). Solid lines are theoretical predictions with slopes q. For $q = 0.2$ ($q = 0.5$) computed relative errors (standard deviation divided by mean) range from 0.3% to 0.1% (0.5% to 0.3%) for the smallest and largest times, respectively. All results are shifted by $A(q)$ to force theoretical intercept to origin. The proximity of numerical and theoretical intercepts is a precise test of the speed c. (b) Exponent $\zeta(q)$ characterizing moments $\langle r^q \rangle \sim t^{\zeta(q)}$. Solid line is theory. $\zeta(q)$ values are measured slopes ($30 < Qt < 300$) for curves of the same type as in (a). The two sets of data represent averages over 5×10^3 and 6×10^4 particle walks (triangles and squares, respectively). Relative errors in measured slopes for 5×10^3 (6×10^4) particles range from 0.2% to 4% (0.2% to 1%) for the smallest and largest displayed q values, respectively.

of 3×10^9 time steps which correspond to $t = 300Q^{-1}$ [23]. Relative errors for the moments shown in Fig. 2(a) are very small (see caption). We have repeated these simulations for a range of parameter values (Q and Qt_h); in all cases the agreement with theory is of a similar quality to that for the parameter values used to generate the data of Fig. 2.

This $r \sim t$ behavior implies that harmonic surface density perturbations of wave vector k relax in a time $\tau \approx (ck)^{-1}$. However, this cannot be the whole story since, according to the Cauchy distribution of Eq. (5), moments $q > 1$ apparently do no exist. In fact, higher moments do of course exist and we find they are governed by a modified Gaussian form to which the Cauchy distribution crosses over at scales of order $(Dt)^{1/2}$. This Gaussian tail represents the very small fraction of molecules, namely,

$(t/t_h)^{1/2}$, which have been lost by the surface after a time t much less than the retention time t_h. These exceptional molecules have made bulk excursions lasting of order t with a corresponding Fickian displacement $r \approx (Dt)^{1/2}$. Adding their contribution to that from the overwhelming majority which have moved anomalously ($r \approx ct$), one finds that for $t \ll t_h$ the high moments are determined by the few released molecules:

$$\langle r^q(t) \rangle \approx (ct)^q + \left(\frac{t}{t_h}\right)^{1/2} (Dt)^{q/2} \sim \begin{cases} t^q, & q < 1, \\ t^{(q+1)/2}, & q > 1. \end{cases} \quad (6)$$

We have confirmed this rather interesting and anomalous scaling of the displacement moments analytically, finding also that the marginal moment $q = 1$ exhibits a logarithmic form, $\langle r \rangle \approx ct \ln(t_h/t) + O(t)$. Our numerical measurements of the exponent $\zeta(q)$, where $\langle r^q \rangle \sim t^{\zeta(q)}$, provide strong support for the predicted anomalous scaling form. The results of Fig. 2(b) suggest convergence to the theoretical values as the number of stimulated particles N increases, and are consistent with the corrections we have found to Eq. (6). These are increasingly serious as $q \to 1$, being of order $(t/t_h)^{|q-1|/2}$. For finite N, an additional systematic error arises when $q > 1$ because $\zeta(q)$ is then dominated by the $N(t/t_h)^{1/2}$ particles making long steps. Correspondingly, for smaller N values, $N < N^* \equiv (t_h/t)^{1/2}$, it can be shown that the measured $\zeta(q)$ is equal to q; only for $N \gg N^*$ does its value cross over to the true $N \to \infty$ result $\zeta = (q + 1)/2$. This explains the tendency, for $q > 1$, of the $\zeta(q)$ curves in Fig. 2(b) to bend upwards for finite N.

Let us stress that these anomalous statistics depend on a finite *waiting time* between successive bulk excursions. Were there no waiting time, $t^{surf} = 0$, the distribution of r values for fixed time t would simply be a 2D projection of the standard 3D Gaussian distribution for a diffusing particle. This is, of course, another Gaussian. Any finite waiting time destroys this Gaussian. In particular, for strong adsorbers at short times almost *all* of the time is spent waiting, $t^{surf} \approx t$, and fixed t is then equivalent to a *fixed* number of excursions [Eq. (3)]. This leads to the Cauchy form of Eq. (5).

This anomalous diffusion contributes both to density relaxation and self-diffusion. An ideal technique to measure the latter is FRAP [4,10,21] where the decay of, say, an induced harmonic wave of labeled molecules is monitored. The measured intensity is proportional to the amplitude of this wave, $S(\mathbf{k}, t)$, plotted in Fig. 3. At times much less than t_h, for large k [$k \gg (Dt)^{-1/2}$], we find $S = \exp\{-ckt\}$ is the Fourier transform of the Cauchy distribution of Eq. (5). Before the Cauchy cusp at $k = 0$ is realized, however, S crosses over to a small k [$k \ll (Dt)^{-1/2}$] form determined by the few molecules which make bulk excursions lasting of order t: $S = 1 - (t/t_h)^{1/2}f(Dk^2t)$, where f is a function analytic at the origin. The difference $1 - S(k = 0, t)$ is the fraction of molecules which have left the surface and scales as $(t/t_h)^{1/2}$. Since $c = D/h$, it follows that the wavelength k^{-1} in a FRAP study must obey

$k^{-1} \ll h$ if anomalous diffusion is to be observed. At the same time, the method [4] requires that this wavelength exceed that of light, $k^{-1} \gtrsim 1$ μm. Viscoelastic measurements at liquid-fluid interfaces suggest $1 \lesssim h \lesssim 10$ μm; the larger of these h values promise observable anomalous self-diffusion. Even more promising are polymer studies at solid surfaces. For example, in the experiments of Ref. [8] the observed diffusion-controlled effects indicate "strong" behavior with t_h of order hours, implying $h \approx 1$ mm.

So far our discussion has been independent of the nature of the second bulk phase. Now when this phase is a solid, since in-surface diffusivities are generally small, we predict that the bulk-mediated mechanism will often dominate the net surface diffusion. However, when the second phase is a fluid, surface viscoelastic effects provide an important alternative route [1,2,15,16]. As an example, for a typical surfactant-stabilized microemulsion droplet of size $b \approx 0.01$ μm, the relaxation time for inhomogeneities in surfactant surface density can be estimated [15] as roughly 10^{-8} sec. This is much smaller than the "anomalous" relaxation time $\tau = bh/D \approx 10^{-5} - 10^{-2}$ sec, taking values [17] $D \approx 3 \times 10^{-6}$ cm^{-2}/sec, and h in the range [1,17] $10^{-5} \lesssim h \lesssim 10^{-2}$ cm. The conclusion is that surface viscoelastic effects will dominate density relaxations at typical liquid-fluid interfaces for submicron scales. However, especially at high coverages we expect that *self-diffusion* in liquid-fluid cases will remain anomalous, since in-surface mobility is then greatly reduced by neighbors. In contrast, the anomalous mechanism provides the opportunity to short circuit the crowded surface via the dilute bulk. The influence of increased surface density arises only through a reduced adsorption rate Q_{ads}; this is a relatively mild effect.

Our main conclusions are as follows. Two broad classes of reversibly adsorbing bulk-surface systems have been identified: "weak adsorbers" and "strong adsorbers." Strong systems exhibit diffusion control in the liquid bulk, a feature observed in many experiments [5,8,17]. We predict that their adsorption-desorption kinetics will frequently provide the primary mechanism for surface diffusion at both liquid-solid and liquid-fluid interfaces. This
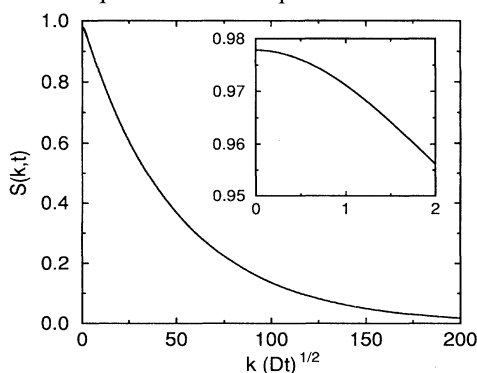
leads to an anomalous "superdiffusive" behavior which is confirmed by detailed numerical simulation: Molecular displacement r grows faster than $t^{1/2}$ for all moments q. Correspondingly, the relaxation of a surface modulation of wave vector k in non-Fickian, $\tau = (ck)^{-1}$, where the speed c is universally related to other observables. Self-diffusion measurements using techniques such as FRAP or forced Rayleigh scattering [24] are promising avenues for the exploration of these unusual effects.

FIG. 3. Correlation function $S(k,t)$ during anomalous regime ($t/t_h = 4 \times 10^{-4}$).

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