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Anomalous diffusion of surface-active species at liquid-fluid and liquid-solid interfaces

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Abstract. — We study the role of bulk-surface exchange in the density relaxation kinetics and self-diffusion of surface-active molecules at liquid surfaces. In « strongly adsorbing » systems, relaxation occurs through bulk-mediated effective surface diffusion characterized by one-step distributions with long tails; molecules execute Lévy walks on the surface. Correspondingly, at times before particles are finally lost to the bulk, surface displacement r is non-Fickian and exhibits anomalous scaling; moments grow as \( \langle r^q \rangle \sim t^{\xi(q)} \), where \( \xi(q) = q \) for \( q < 1 \), \( \xi(q) = (q + 1)/2 \) for \( q > 1 \) and \( \langle r \rangle \sim t \ln t \). The width of an initially localized density disturbance increases linearly in time with a « speed » c which is universally related to other observables. Numerical simulations confirm the family of exponents \( \xi(q) \), and reproduce the observable c. We consider a simple example where end-functionalised macromolecules adsorb at a solid surface, finding \( c \sim 1/s \) where s is the surface « stickiness » parameter. At liquid-fluid interfaces viscoelastic effects compete. For sub-micron scales, we argue that self-diffusion will typically remain dominated at high coverages by the anomalous bulk-mediated mechanism, while surface viscoelasticity will dominate the relaxation of density perturbations.

1. Introduction.

Adsorption-desorption kinetics at interfaces are involved in many phenomena of fundamental and practical importance. Adsorption at the solid-liquid interface arises, for instance, in many biological contexts involving protein deposition [1-3], in solutions or melts of synthetic macromolecules [4-7], in colloidal dispersions [8], and in the manufacture of self-assembly mono and multi-layers [9-12]. Meanwhile, soluble surfactant molecules adsorbing and desorbing at liquid-liquid or liquid-gas interfaces [9, 13-16] are important in the relaxation and collision dynamics of microemulsions, emulsions and foams. In fact, when any liquid containing soluble molecules is brought into contact with a surface for which the particles have a certain affinity, such processes arise.

Amongst the experimental methods suited to the measurement of these kinetics, surface elasticity measurements [17, 18] and pendant drop tensiometry studies [19] have provided valuable information. In general, however, quantitative results are in short supply, though many other methods have the potential to yield further information on kinetics. Examples
include surface light or neutron scattering [20], second harmonic generation [21, 22], ellipsometry [23, 24] and various luminescent techniques such as fluorescence recovery after photobleaching (FRAP) [20, 25] and others [26-30].

This paper is a study of the influence of bulk-surface exchange in the surface density relaxation kinetics and surface self-diffusion in such systems. The role of adsorption-desorption kinetics remains relatively unexplored both experimentally and theoretically. In the various examples mentioned above, surface density inhomogeneities arise (either produced by external agents such as flow or by intrinsic thermal fluctuations) and one would like to establish the relaxation time of, for example, a localized perturbation. A related issue is the time-dependence of the surface displacement of individual adsorbed molecules, i.e. their self-diffusion. There are a number of relevant mechanisms: in-surface diffusion, as at liquid-solid interfaces; surface viscoelastic effects [13, 20, 31-35] in the liquid-fluid cases; and bulk-surface exchange whenever surfactants are soluble. Bulk-surface exchange may lead to effective bulk-mediated diffusion. It is this process, in which particles move from one surface location to another through desorption followed by diffusion in the bulk and adsorption, which is the principal subject of the present study (see Fig. 1). At liquid-solid interfaces, in particular, it is expected in many cases to provide the primary mechanism for both self-diffusion as well as the relaxation of density fluctuations (cooperative diffusion) on timescales before the adsorbed molecules are permanently released to the bulk. Meanwhile, at many liquid-liquid and liquid-gas interfaces we expect self-diffusion to remain dominated by this mechanism at high coverages where in-surface diffusion is heavily suppressed. Experimental FRAP studies of self-diffusion [25] are of particular potential in this respect. In principle, they can provide detailed and accurate surface diffusion information with which to compare the present theoretical work.

![Diagram](image)

Fig. 1. — Particles can move from one surface location to another by desorption followed by diffusion in the bulk and adsorption. Repeated many times, this leads to an effective and anomalous surface diffusion.

With these aims in mind, we will treat a very simple situation in the following: a planar surface contacts a dilute solution of surface-active molecules, at concentration \( p \), which adsorb reversibly at the surface. To begin, we will neglect in-surface mobility and surface
viscoelasticity (these effects will be addressed in Sect. 7), and we seek the relaxation kinetics of the surface coverage \( \Gamma \) (number of molecules per unit area) for small deviations from equilibrium. The relaxation of surface density inhomogeneities is closely related to that of homogeneous perturbations in \( \Gamma \), which involve a net transfer of mass between surface and bulk; these bulk-surface exchange kinetics are of two possible types, depending on the relative magnitudes of the microscopic parameters governing adsorption, desorption and bulk diffusion. We will define « strongly adsorbing » bulk-interface systems as those which retain adsorbate molecules for a sufficient time that « diffusion-control » (DC) onsets in the bulk. In « weak » systems, on the other hand, the desorption time is smaller than that required for bulk DC effects to develop. Strong systems are characterized by slow bulk-surface exchange kinetics, in the sense that the time for the interface to renew its adsorbate population is much greater than the desorption time for a single molecule. Given that molecules are desorbing, and yet are not being permanently lost by the interface, it follows that they must be readsorbing elsewhere on the surface; that is, the interface must be shuffling its occupants around the surface by bulk-mediated effective surface diffusion. Each excursion into the bulk is characterized by distributions of possible times and displacements which turn out to have long algebraic tails; each molecule performs a Lévy walk [36-40] on the surface. The central limit theorem is inapplicable in such cases, and we will find that the net surface displacement for strong systems is correspondingly non-Fickian for times less than the bulk-surface exchange time. In fact, the particle displacement statistics, which at low coverages determine the relaxation of \( \Gamma \), exhibit « anomalous scaling » [41] in that the different moments are governed by a non-trivial family of exponents.

The essential feature of a strong system is that the desorption time is much greater than the « typical » readsorption time during the « anomalous » regime. Thus, a typical molecule spends virtually all of its time on the surface and its bulk-mediated surface displacement is much less than the free Fickian diffusion result: the « sticky » interface strongly retards particle motion. We will show, in fact, that the time spent in the bulk (for most molecules) grows like \( t^2 \) and the surface displacement evolves as \( r \sim t \); the surface density distribution (starting from a localised patch) is a 2-dimensional Cauchy form whose width grows linearly in time. However, an important consequence of the algebraic tails of the step distributions is that a small fraction of molecules make very big jumps, lasting of order \( t \), and suffer Fickian displacement which scales as \( t^{1/2} \). It turns out that this minority determines the higher moments of \( r \).

The emphasis of this paper is on theoretical results. In addition, we have performed extensive numerical simulations which have substantiated our predictions. Some of these results, which provide strong support for the anomalous scaling, are presented in the following. Details will appear elsewhere [42].

The paper is structured as follows. In section 2 the definitions of « weak » and « strong » are made precise, and in section 3 the relaxation of surface density inhomogeneities is introduced. Weak systems relax such perturbations in a single desorption time, simply replacing the old population with a new one, while strong systems are subject to the anomalous diffusion described previously and for short times exhibit a non-Fickian relaxation spectrum, \( \tau_\kappa \sim 1/k \) for surface wave-vector \( \kappa \). The remaining sections specialize to strong systems and follow the motion of a single molecule, or equivalently the spreading out of an initially localized patch of surface density excess or deficit. In sections 4 and 5 we study the long-tailed distributions of total time elapsed and total displacement, respectively, after \( n \) excursions into the bulk, i.e. after \( n \) steps of the molecule’s Lévy flight. Numerical results are presented which corroborate the theoretical picture. Section 6 deals with those properties corresponding to experimental observables, namely the statistics of the displacement \( r \) after a given time.
2. « Weak » and « strong » adsorbers.

The simplest description of an adsorbing-desorbing interface interacting with a dilute bulk must invoke the bulk diffusivity $D$, a characteristic desorption time $Q^{-1}$, a surface « capture range » $b$ and surface adsorption time $Q_{ads}^{-1}$. These last two define an adsorption « sink » of width $b$ and strength $u = Q_{ads} b$. To appreciate the meaning of « weak » and « strong », consider firstly the pure adsorption case ($Q = 0$); the interaction of the bulk with the interface is then a 1-d reaction-diffusion problem (ignoring transverse variations for simplicity). Reaction kinetics in 1-d exhibit « diffusion-controlled » (DC) behaviour in consequence of the compactness of the spatical exploration of a particle [43, 44]. This is a true statement, at large enough times $t$, even for a very weak reaction sink: one can say that kinetics are driven to DC form by increasing $t$. The cross-over time, $t^*$, is estimated by equating to unity the adsorption probability of a particle close to the interface (i.e. within a range $\approx \sqrt{Dt^*}$):

$$\int_0^{t^*} dt \left( \frac{t}{t_b} \right) \frac{b}{(Dt)^{1/2}} Q_{ads} t_b \approx 1,$$

in which $b/(Dt)^{1/2}$ is the fraction of « steps » (each lasting $t_b$) which lie adjacent to the interface, during each of which the adsorption probability is roughly $Q_{ads} t_b$. This implies

$$t^* = (r^*)^2 / D, \quad r^* = 2D/u,$$

where $r^*$, the diffusion length associated with $t^*$, is the « renormalized » sink size (the factor of 2 is introduced for convenience). That is, coarse-grained over the scales $r^*$ and $t^*$ in space and time, kinetics are « perfectly adsorbing »; any particle which strays to within $r^*$ of the interface almost certainly « reacts ». Clearly then, an initially homogeneous bulk must develop a hole of size $\sqrt{Dt}$ for $t > t^*$, and delivery of material to the interface becomes controlled by diffusion.

Switching desorption back on, if it happens that $Q^{-1} \gg t^*$ the DC behaviour described above has had time to develop before the surface releases any adsorbed particles, and one anticipates serious bulk disturbance in response to a surface perturbation. This is our definition of a « strong » adsorber, $Qt^* \ll 1$. In a « weakly adsorbing » system, $Qt^* \gg 1$, desorption onsets before a bulk hole has developed; the bulk remains close to equilibrium and this governs the delivery of material to, for example, a bare surface. As we will demonstrate, this phenomenology is indeed exhibited by the following bulk-interface dynamics, where $r = (x, y, z)$ and $x$ is the coordinate orthogonal to the planar surface, $x = 0$:

$$\dot{p} - D \nabla^2 p = -u\delta(x)p + Q\delta(x) \Gamma$$

$$\dot{\Gamma} = -Q\Gamma + up \delta$$

Here $p^s = p(x = 0)$ is the bulk concentration at the surface, boundary conditions $p(x \to \pm \infty) = p^{\infty}$ pertain, and we use the domain $-\infty < x < \infty$ with initial conditions
symmetric about \( x = 0 \) to mimic reflecting boundary conditions. The sink strength, \( u = Q_{\text{ads}} b \), can then be written as

\[
    u = 2 Q_h, \quad h = \frac{\Gamma^\text{eq}}{p^\text{eq}}, \tag{4}
\]

where \( \Gamma^\text{eq} \) is the equilibrium surface coverage corresponding to \( p^\text{eq} \). Physically, the «adsorption depth » \( h \) corresponds to the amount of bulk required to fill an empty surface. Generally, \( p \) and \( \Gamma \) should be interpreted as deviations from the equilibrium values, equation (3) is then valid provided these deviations are small, and \( h \) is more generally defined to be the slope of the equilibrium adsorption isotherm.

Consider an initially empty bulk and homogeneous surface \((\Gamma = \Gamma^0, p = 0)\). Equation (3) is then easily solved by Laplace transforming, \( t \rightarrow E \):

\[
    p_E(x) = \Gamma^0 \frac{g_E(x)}{1 + E/Q + \sqrt{Et_h}}, \quad \Gamma_E = \frac{\Gamma^0}{E} \frac{E/Q + \sqrt{Et_h}}{1 + E/Q + \sqrt{Et_h}}, \tag{5}
\]

where \( g_E(x) = (4 E D)^{-1/2} \exp(-x(E/D)^{1/2}) \) is the bulk diffusion Green's function and \( t_h = h^2/D \) the diffusion time corresponding to the adsorption depth. This time-scale will feature prominently in what follows; in fact «strong» and «weak» can equivalently be defined as \( Q t_h \gg 1 \) and \( Q t_h \ll 1 \) respectively since equation (2) implies

\[
    Q t^* = \frac{1}{Q t_h} \tag{6}
\]

It is now straightforward to demonstrate that equation (5) reproduces the «no-desorption» reaction kinetics discussed above in the domain \( E/Q \gg 1 \). Our main interest, however, is in longer times when the \( E/Q \) term can be dropped. Then for time-scales much less than \( t_h \), or \( Et_h \gg 1 \), the inverse Laplace transform of the expression in equation (5) yields diffusion-controlled behaviour

\[
    p(x, t) \approx \frac{\Gamma^0}{h} \text{erfc} \left( \frac{x}{2 \sqrt{Dt}} \right), \quad \Gamma(t) \approx \Gamma^0 \left[ 1 - \left( \frac{t}{t_h} \right)^{1/2} \right] (Q^{-1} \ll t \ll t_h). \tag{7}
\]

Clearly, the above regime only exists for a strong adsorber \((Q t_h \gg 1)\). The response in the case of a weak system is very different; then the sequence of time scales reads \( t_h \ll Q^{-1} \ll t^* \) and for times less than \( t^* \) \((Et^* \gg 1)\) one can discard the \( \sqrt{Et_h} \) terms in equation (5) (being much less than \( E/Q \)) and one finds exponential recovery, \( \Gamma - \Gamma^\text{eq} \sim e^{-Qt} \) with the bulk almost unaffected, \( p = p^\text{eq} \). Thus the relaxation time for weak systems is \( Q^{-1} \); the surface has completely recovered before any DC effects can occur.

Returning to the «strong» result, equation (7), one can say that for times much less than \( t_h \) the relative number of solute particles on the surface is virtually unchanged and a front of desorbed particles extends \( \sqrt{Dt} \) into the bulk. Unlike a weak system, the surface holds onto its initial occupants well beyond the desorption time \( Q^{-1} \); exchange kinetics with the bulk are very slow, requiring a time \( t_h \) for completion as can be deduced from equation (5) for
$Et_h \ll 1$ when one finds that $\Gamma$ and $p$ have recovered their equilibrium levels. The relaxation time is $t_h$.

Why does the surface (for strong cases) retain its occupants during the regime $Q^{-1} < t < t_h$? Roughly, equation (1) defines $t^*$ as the readsorption time: since $t^* \ll Q^{-1}$, particles spend almost all on the time of the surface during a sequence of desorptions and readsorptions. At any instant, therefore, nearly all of the initial population must be on the surface even for $t \gg Q^{-1}$ However, this statement is rather loose; in fact (see Sect. 4) the distribution of readsorption times, $\tau$, has a long $\tau^{-3/2}$ tail and $t^*$ is merely the median time (the mean does not exist). This tail eventually dominates, and particles leave the surface as follows. After $n$ hops on the surface (i.e. $n$ desorption-readsorption events) the number of hops for which the time spent in the bulk lies between $\tau$ and $\tau + d\tau$ is approximately $n(t^*/\tau)^{3/2} (d\tau/t^*)$. The total time spent in the bulk, $t^{\text{bulk}}$, therefore obeys

$$\int_{t^*}^{\tau^{\text{bulk}}} \frac{d\tau}{t^*} n \left( \frac{t^*}{\tau} \right)^{3/2} \tau \approx t^{\text{bulk}},$$

whence

$$t^{\text{bulk}} = n^2 t^* \quad (n \gg 1).$$

The sum is dominated by the small number of excursions (of order unity) into the bulk whose duration is of the same order as the total time, $t^{\text{bulk}}$. Comparing $t^{\text{bulk}}$ with the total time spent on the surface, $nQ^{-1}$, one deduces that for small enough times (and $n$) the fraction of time spent on the surface is virtually unity, but the surface loses its particles when the number of steps reaches a value $n \approx Q t_h$ or $t \approx t_h$.

In summary, there are two natural candidates for the interface relaxation time: the desorption time $Q^{-1}$, and the diffusion time $t_h$ required to transport enough mass from the bulk to restore surface equilibrium. For weak systems the relaxation time is the former, for strong systems the latter.

3. Relaxation of surface density inhomogeneities.

The previous section suggests that spatial variations in $\Gamma$ should relax very differently in the weak and strong cases. Let us follow the evolution of an initial harmonic surface wave, $\Gamma = F_0 e^{kk}r$ ($r$ and $k$ lying in the surface) confronted by an empty bulk. Equation (3) can be solved to give [45]

$$\Gamma_{E_k} = \frac{E/Q + EhS_{E_k}}{1 + E/Q + EhS_{E_k}} \frac{F_0}{E},$$

in which the transform of the « return probability » [45] satisfies

$$EhS_{E_k} = \sqrt{Et_h} \left( \frac{E\tau_k}{1 + E\tau_k} \right)^{1/2} \approx \begin{cases} E / \sqrt{Et_h}, & E\tau_k \ll 1, \\ \sqrt{E\tau_k}, & E\tau_k \gg 1, \end{cases}$$

where $\tau_k = 1/Dk^2$ is the Fickian relaxation time. Motivated by our previous observations, let us examine wavectors in the range $t^* < \tau_k < t_h$ (which only exists for a strong system). In the bulk, of course, such a wave would have relaxed by $t \approx \tau_k$; in contrast, by choosing $E\tau_k \gg 1$ in equation (10), one can show that the surface wave is little changed from its initial amplitude on these time scales. We will see later that this is due to the « clinging » effect of the
surface which reduces the surface displacement after time $\tau_k$ to a value much less than $k^{-1}$. Relaxation in fact proceeds on a much longer scale; from equations (10) and (11) one finds

$$\Gamma_k(t) \approx \Gamma_k^0 e^{-t/\tau_k} \quad (t \gg \tau_k), \quad \text{(12)}$$

where the «anomalous» relaxation time is

$$\tau_k \approx \sqrt{\tau_k} t_k \equiv (ck)^{-1} \quad \text{(13)}$$

and is characterized not by a diffusion constant but rather by a «speed» $c$,

$$c \equiv \frac{D}{h} \quad \text{(14)}$$

The harmonic surface imprint is remembered for much longer than the bulk memory time, $\tau_k$. This is a very different decay to that for the weak case which one can demonstrate to be independent of wavevector, $\Gamma_k \sim e^{-Qt}$. The surface loses its harmonic wave after a single desorption time.

Corresponding to this anomalous surface relaxation is an unusual development of the bulk field $p_k(x)$. Specialising to the same $k$ values and times greater than the desorption time, one can show [45] that the bulk is locally equilibrated with the surface ($hp_k(x = 0) = \Gamma_k$) and the surface influences the bulk up to a penetration depth $\sim k^{-1}$.

$$p_k \approx \frac{\Gamma_k^0}{h} e^{-kt} \quad e^{-t^2} \quad (t \gg \tau_k) \quad \text{(15)}$$

The total mass in the bulk for a given value of $r$ is much less than the amount on the surface at that point, by a factor $1/kh$.

Let us translate into real space. In particular, we ask how a localized patch of excess surface density «spreads» on the surface in a strong adsorber. Provided the initial patch dimension is much less than $h$, «spreading» is a reasonable term since we know the surface retains particles up to $t_k$. Now the expression of (12) is precisely the Fourier transform of the Cauchy distribution [46, 47]. Since its validity in $k$-space is restricted to $k^{-1} \ll \sqrt{Dt}$ for a given time $t$, one can justifiably transform to $r$ provided the result is only interpreted on corresponding scales:

$$\Gamma (r, t) \approx \frac{1}{2 \pi} \frac{ct}{[(ct)^2 + r^2]^{3/2}} \quad (r \ll (Dt)^{1/2} \quad t \ll t_k) \quad \text{(16)}$$

Equation (16) describes a patch which remains attached to the surface and grows linearly in time with «speed» $c$. The patch density follows a 2-d Cauchy distribution, falling off slowly at large distances, $\Gamma \sim 1/r^3$, with amplitude at the origin decaying as $\Gamma \sim 1/t^2$. The normalization up to scales $r \sim (Dt)^{1/2}$ is close to unity when $t \ll t_k$ and it is straightforward to show that the contribution from wavevectors $k^{-1} \gg \sqrt{Dt}$ is correspondingly small when $t \ll t_k$. However, the behaviour of $\Gamma$ on the largest scales, $r \gg \sqrt{Dt}$, is in fact of importance despite representing only a small fraction of the surface particles. As will be shown later, it determines the higher moments of $r$.

In a similar manner, the real space bulk profile is obtained as

$$p \approx \frac{1}{2 \pi h} \frac{ct + x}{[(ct + x)^2 + r^2]^{3/2}} \quad (t \ll t_k) \quad \text{(17)}$$
This result is valid only for $x, r < \sqrt{Dt}$. In fact, integrating over transverse coordinates $r$ gives $1/h$ for any value of $x$, and the $x$ integration would then diverge were it not cut off at $x = \sqrt{Dt}$. (The behaviour in $x$ after the $r$ integration is of course just the result (7), viz., the evolution for the case of homogeneous surface coverage, and is cut off by the complementary error function). The effect on the bulk of the initially localized surface perturbation, depicted in figure 2, is thus a right cone extending a distance $\sqrt{Dt}$ both orthogonally $(x)$ and transversally $(r)$. The angle between the interface and the cone edge, $r = x + ct$, is 45°, and the top section of the cone, where it meets the patch of width $ct$, is « cut off » by the surface. For each value of $x$ the profile in $r$ is a Cauchy distribution of width $x + ct$, and each such slice contains the same « mass ».

Fig. 2. — Effect of spreading surface patch on bulk for a strong adsorber at times $t \ll t_\nu$. A slice $y = 0$ is depicted, where $r = (y, z)$ lies in the surface. Most mass is contained in the surface patch whose size grows with « speed » $c$, whilst the mass in the bulk occupies a cone of extent $\sqrt{Dt} \approx ct$ and edge $r = x + ct$. A disk $x =$ Cte. is shown : particles contained in this disk follow a Cauchy distribution in $r$ of width $x + ct$. Each such disk contains equal mass.

In the following sections we will study this bulk-mediated motion of particles on the surface more thoroughly. The Cauchy distribution, equation (16), describes an anomalous non-Fickian effective surface diffusion, $r \sim t$. It will be shown that the distribution on larger scales corresponds to a different but equally anomalous dynamics. A clear picture emerges when one follows the motion of a single initially adsorbed solute particle; such a particle performs a Lévy walk on the surface.

4. Time elapsed after $n$ surface hops : Lévy flight.

We begin by asking how much time has elapsed after a particle, specified to be adsorbed at $t = 0$, has performed $n$ steps on the surface. This and the next two sections will deal exclusively with strong systems. A new « step » begins when a particle is readorsed, continues for the duration of its stay on the surface, continues further as the particle desorbs
and diffuses in the bulk, and terminates at readsorption. The distribution of times for one step, \( \psi(t) \), is characterized by long tails, that is, the particle performs a directed Lévy flight [48] in time.

4.1 One-step distribution of times spent in bulk. — To obtain \( \psi(t) \), one must account both for time on the surface and in the bulk. The distribution of times in the bulk, \( \psi_{\text{bulk}}(t) \), is related to \( \Pi(t) \), the probability a particle starting in the bulk at \( x = 0 \) has been readsorbed by the time \( t \), which is the solution (for \( \Gamma \)) to the one-dimensional version of equation (3) with \( Q \) set to zero and initial conditions \( \Gamma = 0 \), \( p = \delta(x) \):

\[
\Pi(t) = 1 - e^{-t^{*}} \text{erfc} \left( \sqrt{\frac{t}{t^{*}}} \right), \quad E \Pi(E) = \frac{1}{1 + \sqrt{Et^{*}}}. \tag{18}
\]

The probability density that a particle’s excursion into the bulk lasts \( t \) is just the derivative, \( \psi_{\text{bulk}} = \Pi \), which from equation (18) has the long time tail \( (\tau \gg t^{*}) \) mentioned previously, \( \psi_{\text{bulk}} \sim t^{-3/2} \).

It is worth noting that at long times \( \psi_{\text{bulk}} \) exhibits the same behaviour as for a perfectly adsorbing interface with the particle initially at \( x \approx r^{*} \), rather than \( x = 0 \), as may be shown as follows. This latter problem is simply solved by introducing an image (of normalization \(-1\)) at \( x = -r^{*} \); the normalization in the bulk, \( 1 - \Pi_{\text{perf}} \), is then just the difference of the areas (in \( x > 0 \)) of two Gaussians with relative displacement \( 2r^{*} \) which for \( \tau \gg t^{*} \) gives \( 1 - \Pi_{\text{perf}} = r^{*} / \sqrt{D\tau} = (t^{*}/\tau)^{1/2} \). This has the same form as the long time behaviour of equation (18). That the \( \tau \gg t^{*} \) behaviour in our problem, where the sink strength is finite, should reproduce the infinite strength result is expected in view of the discussion of section 2: for times \( \tau \gg t^{*} \) and spatial scales \( r > r^{*} \) the sink is effectively perfectly adsorbing.

4.2 \( n \)-step distribution of times spent in bulk. — Consider firstly the distribution of total amounts of time \( t_{\text{bulk}} \) spent in the bulk after \( n \) steps, \( \psi_{n}(t_{\text{bulk}}) \). The long tail, \( \psi_{\text{bulk}} \sim t^{-3/2} \), immediately tells us that the central limit theorem breaks down and the one-step distribution for bulk excursions belongs to the domain of attraction of the (directed) stable distribution with characteristic exponent 1/2 (Smirnov distribution) [46, 48]. To see this, let us define the distribution of scaled times as

\[
\tilde{\psi}_{n}(t_{\text{bulk}}/n^{2}) = n^{2} \psi_{n}(t_{\text{bulk}}), \tag{19}
\]

which obeys \( \tilde{\psi}_{n}(E) = \psi_{n}(E/n^{2}) \). In Laplace space the \( n \)-step distribution is just \( [\psi_{\text{bulk}}(E)]^{n} \), whence

\[
\tilde{\psi}_{n}(E) = e^{-n \ln (1 + \sqrt{Et^{*}/n^{2}})} = e^{-\sqrt{Et^{*}}} \quad (n \gg 1), \tag{20}
\]

where equation (18), was used. This gives the Smirnov distribution [49] with characteristic scale \( n^{2} t^{*} \),

\[
\psi_{n}(t_{\text{bulk}}) = \frac{(4 \pi t^{*})^{-1/2}}{n^{2} t^{*}} \left( \frac{n^{2} t^{*}}{t_{\text{bulk}}} \right)^{3/2} e^{-n^{2} t^{*}/4}, \tag{21}
\]

in accord with the argument of section 2, where it was found that the characteristic value of \( t_{\text{bulk}} \) was \( n^{2} t^{*} \). The above simplified derivation of \( \psi_{n} \) is made rigorous in the theory of stable distributions [46]. In conclusion, the distribution of total times spent in the bulk has a long tail, just as for the one-step distribution.
4.3 n-STEP DISTRIBUTION OF TIMES SPENT ON SURFACE. — Since a particle desorbs with constant probability \( Q \) per unit time, the distribution of residence times is \( Q e^{-Qt} \). Having no long tail, the central limit theorem is now applicable. Indeed, if one repeats the procedure used to obtain \( \psi_n^{\text{bulk}} \), but replaces \( n^2 \rightarrow n \), it is straightforward to show that the one-step distribution is driven to a simple delta function after \( n \gg 1 \) steps, \( \delta(t - nQ^{-1}) \).

4.4 n-STEP DISTRIBUTION OF TOTAL TIMES ELAPSED. — Having derived \( \psi_n^{\text{bulk}} \), the one-step distribution of total times elapsed is immediately obtained as

\[
\psi(t) = \int_0^t dt' Q e^{-Q t'} \psi_n^{\text{bulk}}(t - t').
\]

(22)

It follows that the \( n \)-step distribution, \( \psi_n(t) \), of total times elapsed is driven to the product of the above Smirnov and delta functions in Laplace space. In real space, therefore, \( \psi_n(t) \) is the Smirnov function shifted by \( nQ^{-1} \), and vanishing for \( t < nQ^{-1} \):

\[
\psi_n(t) = \psi_n^{\text{bulk}}(t - nQ^{-1}) \theta(t - nQ^{-1}).
\]

(23)

Provided one can ignore the long tail (which is permissible only for moments \( q < 1/2 \)) then the above \( n \)-step distribution of times is essentially a delta function, i.e. one has \( t = nQ^{-1} \) for such lower moments. The distribution is illustrated in figure 3. Thus (in some sense) a particle spends most of its time on the surface provided \( n \ll 1/Qt^* \) or equivalently \( t \ll t_h \). For larger \( n \) and \( t \), the width of the «cut-off» region of the Smirnov distribution (the median total time spent in the bulk) becomes larger than the time spent on the surface, \( n^2 t^* \gg nQ^{-1} \). However, such statements are loose: in fact any moment \( \langle t^q \rangle \) for \( q \geq 1/2 \) does not exist, i.e. is dominated by long bulk excursions. The preceding remarks are thus meaningful only in reference to sufficiently small moments.

Fig. 3. — Distribution of times elapsed after \( n \) steps for a strong system. The case \( t \ll t_h \) is shown for which the time spent on the surface is much greater than the time spent in the bulk: \( nQ^{-1} \gg n^2 t^* \).
To test the above predictions and those which follow, we have measured [42] the bulk-mediated spreading of particles in a number of lattice computer simulations for a range of strong systems. Particles simply random walk on the cubic lattice and adsorb/desorb with probabilities per unit time $Q_{ads}$ and $Q$ respectively. These latter are varied to give a range of « strengths » as measured by $Q_{t_h}$ (the reader is referred to Ref. [42] for details). In figure 4a, total times elapsed $versus$ number of surface hops $n$ are shown for a strength $Q_{t_h} = 6 \times 10^3$, as measured by the moment $q = 1/4$. The anticipated linear relationship, $t \sim n$, is almost exactly reproduced.

Fig. 4. — Numerical results for $Q_{t_h} = 6 \times 10^3$. (a) $Q \langle r^{1/4} \rangle$ as a function of number of steps $n$ for $q = 1/4$ ($\bullet$). The linear dependence expected for times much less than $t_h$ (see text) is shown for comparison (solid line). (b) $\log (\langle r^{q/2} \rangle / r^{q/2})$ versus $\log n$ for $q = 0.2$ (+) and $q = 0.5$ (□). Solid lines are theoretical predictions (having slopes $q$). All results are shifted by the $q$-dependent constant $A(q)$ to force theoretical intercept to origin (see Ref. [42] for details). (c) $\log (\langle r^{q/2} \rangle / r^{q/2})$ versus $\log Q_t$ for the same $q$ values as in (b). Results are again shifted by $A(q)$. The coincidence of numerical and theoretical intercepts is a precise test of the speed $c$. 
To summarize this section, the total time elapsed after \( n \) steps scales at \( t \sim n \) for times smaller than \( t_h \), and at \( t \sim n^2 \) for times greater than \( t_h \), provided one considers sufficiently low moments. In section 6 we will see that this \( t \sim n \) relation plays a crucial role for lower moments of the anomalous surface displacement, while higher moments are governed by the long \( t^{-3/2} \) tail of the distribution of total times spent in the bulk.

5. Displacement on surface after \( n \) hops: Lévy flight.

In this section we forget about time, seeking the particle’s displacement after \( n \) steps. We will show that the displacement grows linearly with the number of steps, \( r \sim n \), provided one considers moments lower than the first. This, too, is a consequence of a long tail one-step distribution; a symmetric Lévy flight [47] is executed. The one-step distribution of surface displacements is simply related to the bulk time distribution through the two-dimensional diffusion Green’s function:

\[
\psi(k) = \int_0^\infty d\tau \, \psi_{\text{bulk}}(\tau) e^{-Dk^2 \tau}
\]  

(24)

Observing that the Laplace transform of the integrand is \( \psi_{\text{bulk}}(E + Dk^2) \), the use of equation (18) leads to

\[
\psi(k) = \frac{1}{1 + kr^*}.
\]

(25)

Clearly, the variance of the above distribution \((- \nabla^2_k \psi \mid_{k = 0})\) does not exist, so when iterated the central limit theorem does not apply. The small \( k \) behaviour \( (\psi \sim 1 - kr^*) \) indicates that \( \psi(r) \) belongs to the domain of attraction of the (symmetric) stable distribution with characteristic exponent 1 (Cauchy distribution). The small and large \( k \) behaviours imply \( \psi(r) \sim 1/r \) for \( r \ll r^* \), \( \psi(r) \sim 1/r^3 \) for \( r \gg r^* \). (In fact explicit inverse transform of equation (25) is possible in terms of the zeroth order Struve and Neumann functions [50].)

As we would expect, for \( r \gg r^* \) the one-step distribution \( \psi(r) \) is the same as for a surface of infinite adsorbing strength given an initial particle location at \( x = r^* \). (In this case, using an image sink at \( x = - r^* \), the \( 1/r^3 \) behaviour emerges as the field of an electric dipole.) For our finitely adsorbing case, the particle « bounces » many times on the surface, moving a distance of order \( r^* \) before it gets adsorbed.

Before formally deriving the \( n \)-step distribution \( \psi_n(r) \), let us estimate the displacement after \( n \) steps using some simple but physically revealing arguments. For this purpose, consider firstly a general distribution with characteristic exponent \( \alpha \) in \( d \)-dimensional space, \( \psi(r) \sim r^{-\alpha} \). Then the probability distribution for \( |r| \) behaves like \( p(r) \sim r^{-1-\alpha} \) and after a total of \( n \) steps the number of steps having size of order \( r \) is roughly \( n(r^*/r)^\alpha \). An estimate of their contribution to the total displacement is

\[
d(r) \approx \left[ n \left( \frac{r^*}{r} \right)^\alpha \right]^{1/2} r \sim r^{1-\alpha/2}
\]  

(26)

since the \( n(r^*/r)^\alpha \) steps are randomly ordered. For \( \alpha > 2 \), the smallest scales, \( r \approx r^* \), are dominant and the total displacement is approximately \( d(r^*) \approx n^{1/2} r^* \). This is the central limit theorem. However, for long tails, \( \alpha < 2 \), the largest scales dominate, namely \( r \approx r^\text{tot} \), where \( r^\text{tot} \) is the total displacement. That is, the size of the biggest steps (of which there are order unity in number), and the total displacement are one and the same: \( d(r^\text{tot}) = r^\text{tot} \). Thus

\[
r^\text{tot} = n^{1/\alpha} r^* \quad (\alpha < 2)
\]

(27)
Applying this to the present case, for which $\psi \sim 1/r^3$ in $d = 2$, that is $\alpha = 1$, one expects linear growth $p^{\text{tot}} \sim n$.

To demonstrate this linear behaviour in a more concrete way, let us calculate $\psi_n(r)$ explicitly. Analogously to equation (19), we define the distribution of scaled total displacements as $\hat{\psi}_n(r/n) = n^2 \psi_n(r)$, implying $\hat{\psi}_n(k) = \psi_n(k/n)$. Once again, the $n$-step distribution in reciprocal space is $\psi^n(k)$, and using equation (25) one has

$$\hat{\psi}_n(k) = e^{-n \ln (1 + k r^*/n)} \approx e^{-k r^*} \quad (n \gg 1).$$

This leads to a Cauchy distribution of width $n r^*$ on the surface,

$$\psi_n(r) = \frac{1}{2\pi} \frac{n r^*}{(n r^*)^2 + r^2)^{3/2}},$$

exhibiting the expected $r \sim n$ and, asymptotically, $1/r^3$ behaviour. The numerical results [42] of figure 4b, obtained for the same parameter values as figure 4a, are in close agreement with the moments for $q = 0.2$ and $q = 0.5$ as deduced from equation (29), after a transient of about 10 steps.

Naïvely, the $t \sim n$ and $r \sim n$ behaviours which have been established in this and the preceding section, respectively, suggest the $r \sim t$ dynamics of section 3. However, the relationship between statistics at fixed $n$ and at fixed $t$ is rather subtle and will be clarified in the next section. Clearly, these are fundamentally different. For instance, according to equation (29) moments of $r$ for $q \gg 1$ do not exist, for a fixed $n$; the origin of this is the long tail in the bulk time distribution, equation (21). In contrast, for a given time $t$ the time in the bulk cannot, of course, exceed $t$ itself; correspondingly, one can show that all moments of displacement exist at fixed $t$.

6. Displacement after time $t$: Lévy walk.

Experimental observables correspond, of course, to specifying time rather than number of steps. Our aim in this section is the particle displacement after time $t$ which results from its Lévy walk on the surface. That is, we wish to determine the surface density distribution $\Gamma(r, t)$ for a delta-function initial condition.

Before deriving the walk statistics, a simple argument helps connect the fixed $n$ and fixed $t$ relationships. The argument which follows suggests $r \sim t$ and $r \sim t^{1/2}$, for $t$ respectively less than and greater than $t_h$. We remind the reader that $t_h$ is the timescale after which the interface in a strongly adsorbing system loses its occupants. Let us imagine a « transparent » surface, such that after a time which we (suggestively) name $t^\text{bulk}$, the particle (initially located at $x = 0$) would have visited a region of size $r = r^*(t^\text{bulk}/t^*)^{1/2}$ and its trajectory would have intersected the « renormalized » surface (of width $r^*$) of order $n \approx (t^\text{bulk}/t^*)^{1/2}$ times. Switching back on desorption and adsorption, this corresponds to an $n$-step walk with a time $t^\text{bulk}$ spent in the bulk and a net surface displacement $r$. Thus $r \approx nr^*$, $t^\text{bulk} \approx n^2 t^*$ and the total surface residence time is $t^\text{surf} \approx nQ^{-1}$. For $t < t_h$, therefore, the total time $t$ is approximated by $t^\text{surf}$ and we recover $r \approx ct$ with $c = Qr^* = D/h$. In contrast, for $t > t_h$ one has $t = t^\text{bulk}$, leading to the familiar Fickian result $r = r^*(t/t^*)^{1/2}$. We remark that the essential component of this argument is the coarse-graining over scales $r^*$ and $t^*$ after which the surface is, effectively, perfectly adsorbing.

Now in section 3 the distribution of surface displacements $\Gamma(r, t)$ during the anomalous regime $t \ll t_h$ was derived. This was the distribution of equation (16); particles spread out on the surface with a Cauchy distribution of growing width $ct$. Accordingly, the $q$-th moment
\[ \langle r^2(t) \rangle \text{ apparently exists only for } -2 < q < 1. \text{ This conclusion is actually in error, since the Cauchy result was derived for displacements much less than the Fickian scale } \sqrt{D t}; \text{ for larger scales the true decay is strong enough to render the } q > 1 \text{ moment existent. One can verify this by starting from the exact expression for } \Gamma \text{ in Fourier-Laplace space of equation (10), with initial condition } \Gamma_0^{(0)} = 1, \text{ after coarse-graining over the scales } Q^{-1} \text{ and } r^* \text{. Evaluating, for example, the second derivative at } k = 0 \text{ one finds that the second moment exists and is given by}
\[
\langle r^2 \rangle = D t \left( \frac{t}{t_h} \right)^{1/2} \quad (t \ll t_h).
\]

This is reduced from the Fickian expression by the factor \((t/t_h)^{1/2}\). This factor is the fraction of particles off the surface at time \(t\), most of which are a distance of order \(\sqrt{D t}\) into the bulk (see Eq. (7)). Each such particle is therefore in the middle of a « long » excursion lasting of order \(t\). Thus it follows that a fraction \((t/t_h)^{1/2}\) of particles have executed such long excursions by the time \(t\), each of which leads to a displacement of order \(\sqrt{D t}\) on the surface. These exceptional events contribute the amount displayed in equation (30) to the second moment. We will see below that this contribution exceeds that from the \(r \sim t\) part.

In order to obtain a complete picture for the \(q > 1\) moments, it is easier to deal with real space. We need the full expression for \(\Gamma(r, t)\) (beyond the Cauchy result referring only to scales \(r < (Dt)^{1/2}\)). In fact, the Smirnov distribution of total amounts of time spent in the bulk after \(n\) steps, equation (21), can provide us with such an expression for \(\Gamma(r, t)\) if we make use of the fact that the time spent on the surface is related to the number of steps as \(t_{\text{surf}} = n Q^{-1}\). Where long tails are involved such equations are in general dangerous; however the (exponential) distribution of surface desorption times is well-behaved, being driven to \(\delta (t_{\text{surf}} - n Q^{-1})\) under iteration. That is, it is permissible to replace \(n\) by \(Q t_{\text{surf}}\) in virtually any expression. Making this replacement in the Smirnov distribution, writing \(t_{\text{surf}} = t - t_{\text{bulk}}\) and summing over all possible values of total times spent in the bulk, \(t_{\text{bulk}}\), one has
\[
\Gamma(r, t) = \int_0^t \text{d}t_{\text{bulk}} \ p(t_{\text{bulk}} | t) \ e^{-r^2/4 D t_{\text{bulk}}},
\]
where the probability density of the bulk time \(t_{\text{bulk}}\) given total time \(t\) is
\[
p(t_{\text{bulk}} | t) = \frac{(4 \pi)^{-1/2}}{t_h} \frac{1}{t_{\text{bulk}}^\text{min} (1 - t_{\text{bulk}}/t)^2} \ e^{-i_{\text{bulk}}^\text{min} (1 - t_{\text{bulk}}/t)^2/4 t_{\text{bulk}}},
\]
and
\[
t_{\text{bulk}}^\text{min} = t^2/t_h.
\]

We have used the properties of the bulk Gaussian propagator which imply the same distribution of distances for a given \(t_{\text{bulk}}\), regardless of how \(t_{\text{bulk}}\) may have been subdivided amongst the \(n\) steps. Note that the distribution of bulk times decays rapidly to zero for times less than the scale \(t_{\text{bulk}}^\text{min}\), which in effect is the minimum time in the bulk for a given total time \(t\) \((t_{\text{bulk}}^\text{min} = n^2 t^* \text{ with } n = Q t)\).

A rigorous derivation of equation (31) is presented in the appendix. There it is shown that this result is valid for times and lengths much greater than the natural coarse-graining scales \(r^* \text{ and } t^*\), and for times much greater than the duration of one step. This is to be expected since our argument above used the asymptotic many-step Smirnov result. Note that the argument specifically refers to those particles which are adsorbed at the time \(t\).

For length scales less than \(\sqrt{D t}\) it is now straightforward to recover from equation (31) the Cauchy form shown in equation (16) for \(\Gamma\). In that case, the integral is dominated by the small
times $t^\text{bulk} \approx t^\text{min}_h$ provided $t^\text{min}_h \ll t$, i.e. provided $t \ll t_h$. On the other hand for $r \gg \sqrt{Dt}$ the Gaussian in equation (31) is always small and the integral is dominated by its upper limit $t^\text{bulk} = t$ (these are the big steps). The width about $t^\text{bulk} = t$ of the Gaussian, $4Dt^{3/2}$, is then much less than that of the other factors, namely $t$. Expanding around $t$, one thus finds for $t \ll t_h$

$$
\Gamma(r, t) \approx \left( \frac{t}{t_h} \right)^{1/2} \left( \frac{Dt}{r^2} \right)^2 \frac{e^{-r/4Dt}}{Dt} \quad (r \gg \sqrt{Dt}).
$$

(33)

After the discussion surrounding the second moment (Eq. (30)), such a form was expected; it refers to the small fraction $(t/t_h)^{1/2}$ of particles which have made big jumps lasting of order $t$. For these, the bulk Fickian diffusion governs displacement and their distribution is correspondingly a function of $r^2/Dt$ closely related to the Gaussian.

We can now deduce the complete family of moments, $\langle r^q \rangle$. This may be done using the above expressions for $\Gamma(r/t)$ in which case one finds the Cauchy $r \ll \sqrt{Dt}$ behaviour dominates moments $q < 1$ (it has almost all of the normalisation), while $q > 1$ is dominated by $r \gg \sqrt{Dt}$ (corresponding to the non-existence of $q > 1$ Cauchy moments). A clearer route, however, begins from equation (31) which gives

$$
\langle r^q \rangle = I_q \int_0^t \, dt^\text{bulk} \, p(t^\text{bulk} | t)(Dt^\text{bulk})^{3q/2}
$$

$$
= (ct)^q \int_0^{t/t_h} \, dt \frac{e^{-t/4u}}{u^{(3-q)2}} \left[ 1 - \frac{t}{t_h} \frac{u}{u} \right] \quad (34)
$$

where $I_q = 2^q \Gamma(1 + q/2)$ and $\Gamma$ is the gamma function. For $q < 1$ the integral is dominated by its lower limit (which corresponds, in effect, to $t^\text{min}_h$) and one obtains the Cauchy moments:

$$
\langle r^q(t) \rangle = (ct)^q [1 + O((t/t_h)^{1 - q/2})] \quad (q < 1).
$$

(35)

(In fact, moments below $q = -2$ do not exist and for $-2 < q < -1$ the leading correction is of order $t/t_h$.) Figure 4c compares the simulated [42] $r$, for the same parameters and $q$ values at for figure 4b, with the predictions from equation (35). Both the slopes, testing the power, and the intercepts, testing the precise numerical value of the « speed » $c$, are very close to theory. That the numerical value of $c$ should be reproduced is as expected. This point is discussed in section 8.

When $q > 1$, the roles of the upper and lower limits are reversed. Long bulk excursions, $t^\text{bulk} \approx t$, now dominate the integral of equation (34) leading to:

$$
\langle r^q(t) \rangle \approx (t/t_h)^{1/2} (Dt)^{3q/2} [1 + O((t/t_h)^{(q - 1)y/2})] \quad (q > 1).
$$

(36)

An interesting feature is that the correction terms, which in both the $q > 1$ and $q < 1$ cases derive from the non-dominant integral limit, are increasingly serious as $q \to 1$. At the boundary, $q = 1$, the limits become equally important and logarithms arise. Integrating by parts, one finds

$$
\langle r(t) \rangle \approx ct \ln \left( t_h/ct \right) + O(t).
$$

(37)

Equations (35), (36) and (37) describe a rather interesting « anomalous scaling » [41] of the surface displacement $r(t)$. That is, $r(t)$ is described by a family of exponents, $\zeta(q)$, whose members are not trivially related to one another. The computer-measured $\zeta(q)$ is shown in
figure 5 for the same system parameters as in figure 4 and two different values of the total number of particles, N, in the spreading patch. One anticipates that for q > 1 the quality of agreement with theory will increase significantly with increasing N since only a small fraction are responsible for high moments. Indeed, figure 5 exhibits a considerable change between N = 5,000 and N = 60,000. The data are strongly suggestive of convergence to the theoretical ζ(q) as N → ∞. Note that the q = 1 measurements will of course never converge as plotted in figure 5 (see Eq. (37)).

![Figure 5](image_url)

**Fig. 5.** — Exponent ζ(q), ⟨r²⟩ ∼ t⁴(q), as measured numerically for QI₆ = 6 × 10⁵. Data are shown for two values of N, the number of particles in the diffusing cloud, and appear to be converging to theoretical values (solid line).

7. Surface viscoelasticity.

Until now, the only equilibration mechanism considered has been that of bulk-mediated diffusion. While expected to dominate in many liquid-solid cases, the situation at liquid-fluid interfaces is complicated by surface viscoelastic effects which are strongly coupled to the bulk. A surface density inhomogeneity generates elastic restoring forces within the surface which relax the perturbation after a time whose value depends both on the elastic moduli involved and the viscosities of surface and bulk. These effects have been intensively investigated by a number of authors [13, 20, 31-33]. In this section we present a very simplified discussion with the aim of placing our « anomalous » results in context.

Consider a simple surface density wave of adsorbed surfactant molecules, which will induce « Marangoni » stresses according to the surface compression modulus ε = ∫ dσ/dΓ where σ is the surface tension [31]. Given a perturbation of small amplitude δΓ about an unperturbed coverage Γ₀, let us make a very rough estimate of its relaxation time τ as a function of the wavevector k. Generally, the dynamics are complicated by coupling to other modes and surface viscosities ; to simplify matters let us consider firstly the case when the latter are very small. Then the only mechanism for dissipation is the bulk viscosity η.
Now the total amount of surfactant transferred across a unit length in the surface is 
\[ v \Gamma^0 \tau, \] 
where \( v \) is the typical velocity generated in the bulk by the surface stresses \([31]\) \( \partial \sigma/\partial r \). Since the deficit in one wavelength is of order \( \delta \Gamma k^{-1} \) per unit length (in the direction orthogonal to \( k \)), one has

\[ v \approx \frac{\delta \Gamma}{\Gamma^0} \frac{k^{-1}}{\tau} \tag{38} \]

Given that the velocity field penetrates a distance \( \ell_h \) into the bulk of liquid of density \( \rho \), by matching bulk stresses \( (= \eta v/\ell_h) \) and surface stresses \( (= (\partial \sigma/\partial \Gamma) \delta \Gamma k) \), one has \( (v = \eta/\rho) \)

\[ \tau = \left[ \frac{\rho v^{1/2}}{\varepsilon} \right]^{2/3} k^{-4/3} \quad (k \ll k^* \equiv v/\rho v^2) \tag{39} \]

in the small penetration depth limit, \( \ell_h = \sqrt{\nu \tau} \ll k^{-1} \).

Now as one increases \( k \), a wave-vector is reached such that \( \ell_h \) saturates at \( k^{-1} \). The penetration into the bulk cannot extend beyond a distance of order one wavelength. (A simple way to see this is by exploiting the similarity of the steady state Stokes equation to Poisson’s equation, implying that for long times the effect of the velocity wave at the bulk surface is related to the potential due to a harmonic surface charge density distribution. This can be shown to decay with distance \( x \) from the surface as \( e^{-kx} \).) Equating the stresses as before, one now obtains

\[ \tau = \frac{\eta}{\varepsilon} k^{-1} \quad (k \gg k^*). \tag{40} \]

For a typical oil-water system \( (\nu_{\text{oil}} \approx \nu_{\text{water}} = 0.01 \, \text{cm}^2/\text{s}, \quad \varepsilon \approx k_B T \Gamma^0 \) [19], with \( \Gamma^0 \approx 1/(10 \, \text{Å})^2 \), the cross-over wavelength \( k^*^{-1} \) is estimated to be of order \( 0.1-1 \, \mu\text{m} \).

The result of equation (39) has been obtained previously [20] for small surface viscosities at the liquid-gas interface. For the case of identical bulks on either side of the interface, the small wavelength relation of equation (40) was derived by Kramer [32] who showed it to be valid when surface compressional viscosity \( \kappa \) is small compared to bulk viscosity in the sense that \( \kappa k/\eta \ll 1 \). For asymmetric bulks these compression modes are coupled to capillary waves [31]. If we nonetheless use equation (40) as a rough guide, comparison with the dispersion relation for anomalous surface relaxation (Eqs. (13) and (14)) then shows that typically \( D \approx 3 \times 10^{-6} \, \text{cm}^2/\text{s} \) [19], \( h \) in the range of \( 10^{-5} \) [31] to \( 10^{-2} \, \text{cm} \) [19]) for sub-micron scales the relaxation will proceed by the surface elasticity mechanism with surfactant exchange with the bulk being largely irrelevant \( (\tau_{\text{anomalous}}/\tau_{\text{viscoelastic}} \approx 10^3 - 10^6) \).

At these sub-micron scales, however, the parameter \( \kappa k/\eta \) may become substantial at high coverages. For instance, if one uses a value \( \kappa \approx 10^{-4} \, \text{g/s} \) typical of the interfacial systems summarized in reference [20], one has \( \kappa k/\eta \approx 10^3 \) for \( k^{-1} = 0.1 \, \mu\text{m} \) and \( \eta = 10^{-2} \, \text{p} \). One can then estimate \( \tau \) in the opposite limit where bulk viscosity is relatively unimportant simply by equating the in-surface elastic and viscous forces as follows. Since \( \nu \tau \) is the typical displacement of an adsorbed molecule due to the compression wave, and \( \nu \tau k \) the corresponding gradient, the elastic force is roughly \( \kappa v k \). Similarly, the typical viscous force is \( \kappa v k \). This leads to Kramer’s result in the high surface viscosity limit, \( \tau = \kappa/\varepsilon \), giving \( \tau \approx 10^{-5} \, \text{s} \) for the same parameter values used previously.

The conclusion from this rather crude discussion is that surface viscoelastic stresses dominate surface density relaxation at liquid-liquid or liquid-gas interfaces of strongly adsorbing systems, at least for « typical » cases at sub-micron scales. (This conclusion may be
reversed, however, in systems involving highly viscous liquids with viscosities in excess of $10^3 \eta_{water}$.

The story for self-diffusion at liquid-fluid interfaces is in general very different, however. An interesting aspect of the bulk-mediated surface diffusion is its relative insensitivity to the density $\Gamma$ of adsorbed particles. As $\Gamma$ increases, one expects the readsorption probability to decrease; in our language, the sink strength $u$ will be diminished somewhat. However, conventional in-surface diffusion is much more severely affected: at high surface packings molecules are virtually trapped in one position. Thus it appears probable that self-diffusion at high surface densities will often remain dominated by the bulk-mediated mechanism when soluble surfactants are involved.

The conclusions of this section pertain to strong systems. The situation for weak systems is no different, provided one deals with perturbations of sufficiently small wavelength. However, as soon as the estimated relaxation times above attain values of order the desorption time $Q^{-1}$, bulk-surface exchange will once more become dominant. That is, for larger wavelength inhomogeneities, the interface will have renewed its occupants before surface viscoelastic effects have had the chance to develop.

8. Summary.

The main results of this work can be summarized as follows. Adsorbed molecules are retained by « strongly adsorbing » interfaces for a much longer time, $t_h$, than the desorption time, $Q^{-1}$. However, during the period $Q^{-1} < t < t_h$ these molecules are shuffled around on the surface by various mechanisms amongst which is bulk-mediated effective surface diffusion under which the displacement on the surface of a given molecule, $r(t)$, develops in time with anomalous scaling. That is, $\langle r^q(t) \rangle \sim t^{\xi(q)}$ where $\xi(q) = q$ for $q > 1$ and $\xi(q) = (1 + q)/2$ for $q > 1$, with logarithmic corrections at $q = 1$. This scaling is simply understood in terms of $p(t_{\text{bulk}} \mid t)$, the probability density a molecule has spent time $t_{\text{bulk}}$ in the bulk after a total time $t$ (see Eq. (32)). Integrating $p(t_{\text{bulk}} \mid t)$, one sees that the overwhelming majority of molecules have spent a time of order $t_{h}^{\text{min}}$ in the bulk; each of these thus moves approximately $(D t_{h}^{\text{min}})^{1/2} = ct$ on the surface. A small fraction, namely $\int_\lambda t_{\text{bulk}} p(t_{\text{bulk}} \mid t) \approx (t/t_h)^{1/2}$ (where $\lambda$ is a constant of order unity), have made big jumps lasting of order $t$ which displace the molecule a distance approximately equal to $(D t)^{1/2}$. For times $Q^{-1} \ll t \ll t_h$, the overall mean $q$-th power of the displacement is therefore

$$\langle r^q(t) \rangle = (D t)^{q/2} \left( \frac{t}{t_h} \right)^{1/2} + (c t)^q \sim \begin{cases} t^q, & q < 1, \\ \frac{t}{\lambda (q + 1)^2}, & q \geq 1 \end{cases}$$

and is dominated at large $t$ by one or the other of the sub-populations, depending on the value of $q$. A typical molecule spends virtually all of its time on the surface. However, the typical time in the bulk, $t_{h}^{\text{min}} = t^2/t_h$, grows with $t$ and the above situation persists until eventually $t_{h}^{\text{min}}$ becomes of order $t$ itself, i.e. the surface loses its molecules. This occurs at $t = t_h$, after which point typical excursions last time $t$ and Fickian statistics are recovered.

During the anomalous regime, low moments and the surface (Cauchy) distribution itself are characterized by the speed $c$. This non-Fickian evolution results from the typical behaviour: most particles spend almost all of their time on the surface for $t \ll t_h$. Thus the typical total time spent in the bulk, $n^2 t^* \ast$, is obtained by setting $n = Q t$; this gives $t^2/t_h$, which is what we have called $t_{h}^{\text{min}}$, and is (self-consistently) much less than $t$ when $t \ll t_h$. Thus $r = (D t_{h}^{\text{min}})^{1/2} = ct$.

We predict that $c$ is universally related to other observables: $c = D/h$ where $h$, being the slope of the equilibrium isotherm, $h = \partial \Gamma / \partial \rho$ at $\rho = \rho^a$, is directly measurable. Given $D$ and
\( h \), a specific numerical value of \( c \) is thus predicted for real experiments, regardless of the detailed surface interactions. There are several reasons to believe this. Firstly, our results were derived using a delta-function surface source and sink (Eq. (3)), which one expects to be the universal large scale source-sink function [51-53] to which other forms would be driven under coarse-graining. Secondly, the very fact that \( c \) (as deduced from the delta-function sink) does not explicitly involve any non-observable properties of the sink function or the desorption process (namely, \( u \) and \( \theta \)) is suggestive of \( c \) being quite generally independent of such details. Lastly, the numerical results presented in previous sections have provided strong support for the relation \( c = D/h \). The precise numerical value of \( c \) was reproduced to within an accuracy of 20\%, despite the fact that the surface sink in the simulations is determined by the details of the lattice employed, and is far from a \( \delta \)-function.

What are the experimental implications of these results? Few measured values for \( t_h \) and \( \theta \) are available, but the indications from studies on surfactant molecules at liquid-liquid and liquid-gas interfaces (e.g. pendant drop tensiometry [19] and surface elasticity measurements [17]) and from measurements of polymer desorption at solid surfaces [7] are that the behaviour is often «strong» (\( Q_t > 1 \)), with \( t_h \) values spanning many orders of magnitude. This is not surprising, given the exponential dependencies of adsorption and desorption rates on surface free energy barriers. As far as anomalous surface density relaxation is concerned, the most relevant application is probably at solid interfaces adsorbent to small molecules, proteins or synthetic macromolecules. As an example, consider a macromolecule possessing one functional group with a strong affinity for the surface. For simplicity, assume ideal behaviour (this would correspond to functionalised polymers dilute in an unfunctionalised melt of otherwise identical chains). Then by considering the equilibrium of those functional groups which are adjacent to the wall and those which are adsorbed, the adsorption depth is determined as

\[
\frac{h}{\rho^{\text{eq}}} = \frac{\Gamma_{\text{eq}}}{\theta^{\text{eq}}} = a e^{W/T} \tag{42}
\]

Here \( a \) is the monomer size and \( W \) the free-energetic advantage of monomer adsorption. Choosing the « capture range » \( b \) to be the polymer coil size \( R \) and recalling the definition of the desorption rate, equation (4), we have \( Q h = \theta \). It follows that the « stickiness » parameter \( s \) is given by

\[
s = \frac{\theta}{\theta} = e^{W/T} \frac{a}{R} \tag{43}
\]

Note that this relation depends only on equilibrium considerations. Let us now assume that due to screening by the melt, statics and dynamics near the surface obey essentially the same scaling laws as in the bulk [54]. Now when the number of chain units \( N \) is large, provided \( W \) is not very small, adsorption is almost certain should the coil stray to within \( R \) of the surface, since many surface-monomer collisions occur during one encounter [53]. Thus (see Fig. 6) \( \theta = 1/\tau \) where \( \tau \) is the bulk coil relaxation time. Using \( D \approx R^2/\tau \), it then follows (see Eqs. (4) and (6)) that the coarse-graining scales \( r^* \) and \( t^* \) are just \( R \) and \( \tau \) respectively, and one finds

\[
\theta t_h \approx s^2 \tau , \quad t_h \approx s^2 \tau , \quad c \approx \frac{R}{\tau} s^{-1} \tag{44}
\]

That is, anomalous surface spreading occurs provided \( s \gg 1 \) or, equivalently, provided \( W/T \) is large compared to \( \ln N \) (since \( a/R \approx N^{-1/2} \)). The surface speed \( c \) varies inversely with the stickiness \( s \).
Fig. 6. — In a melt environment, a macromolecule bearing one group with an affinity for the surface attaches whenever its centre of gravity approaches to within $R$ of the surface. The effective sink strength is $u = R/\tau$ where $R$ and $\tau$ are the coil size and relaxation time.

A similar argument applies for the case when all $N$ monomers adsorb, but now $s$ is exponentially large $[55]$, $s \sim e^{N(\omega/\tau)^2}$ in the ideal case. (In this case, of course, unless concentrations are extremely small the situation will be considerably complicated by many-chain surface effects $[5, 6]$.) Since the desorption rate $Q \sim s^{-1}$ becomes very small, there will be sufficient time spent on the surface for a Fickian in-surface diffusion mechanism to develop (with, say, diffusivity $D_s$). This will compete with the $r \approx ct$ behaviour. Equating $D_s t$ with $(ct)^2$ and remembering that $c = D/h$, one sees that only when $t > (D_s/D_s) t_h \sim s^2$ does the Fickian spreading become overwhelmed by the «anomalous» spreading. When all monomers adsorb, therefore, the anomalous effects would probably be eclipsed for $N \gg 1$ but should be relevant to moderate $N$ values (e.g. proteins).

Finally, at liquid-fluid interfaces, a competing mechanism is that due to Marangoni stresses. For sub-micron scales, we have argued that in typical cases these effects will dominate surface density relaxation, while self-diffusion will derive primarily from the bulk-mediated mechanism.

Appendix.

Calculation of surface distribution $\Gamma(r, t)$.

In this appendix we calculate the surface density distribution $\Gamma(r, t)$ for an initial delta function condition at the origin. The exact solution in $E - k$-space is given by equation (10) with $\Gamma^0_k = 1$. Coarse-graining on scales $Q^{-1}$ and $r^*$ this leads to

$$\Gamma_{Ek} \approx \frac{1}{E + \sqrt{E/t_h + (kc)^2}} = f(E + Dk^2), \quad (A.1)$$

where

$$f(E) = \frac{1}{E + \sqrt{E/t_h - Dk^2}} = g(E + \sqrt{E/t_h}), \quad (A.2)$$
and \( g(E) = 1/(E - Dk^2) \) is just the Laplace transform of the exponential, \( g(t) = \exp(Dk^2t) \). On the other hand,

\[
g(E + \sqrt{Et_h}) = \int_0^\infty dt' e^{-Et'} e^{-\sqrt{Et_h}t'} g(t') .
\] (A.3)

Then, inverse Laplace transforming the product of the two \( E \)-dependent factors in equation (A.3), \( E \rightarrow t \), one obtains \( f(t) \) as an integral containing a convolution of a delta-function and a Smirnov distribution [49] (cf. Eq. (21)). After using equation (A.1), this leads to

\[
I_\kappa(t) = \frac{1}{2\sqrt{\pi}} \int_0^\infty dt' \frac{t-t'}{t_h^{1/2}} \cdot \frac{1}{t'^{3/2}} e^{-(t-t')^2/4t'h} e^{-Dk^2t'} \quad (t < t_h) ,
\] (A.4)

whose inverse Fourier transform is equation (31).

References