

Kinetics of Langmuir Films of Fullerene C60

Allan K. Evans

Department of Mathematical Sciences, De Montfort University, The Gateway, Leicester LE1 9BH, U.K.

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A simplified model of the interaction between Buckminsterfullerene C60 and a water surface is derived. Using this model, we construct a Langevin equation of motion for each fullerene molecule. The rates of various processes occurring in Langmuir films can then be estimated. We consider the rate of escape of molecules from the surface, the rate at which molecules in a monolayer film are promoted to a second layer, and the rate of hopping diffusion in the second layer. These results are used to interpret the published results of experiments with Langmuir films of C60 and to suggest further experiments.

1. Introduction

The unusual properties of C60, or Buckminsterfullerene,^{1,2} have prompted a great deal of research aimed at preparing useful materials. Fullerene-based materials can show high-temperature superconductivity,³ photoconductivity,⁴ nonlinear optical response,⁵ and even some interesting biological properties, such as HIV protease inhibition.⁶ The observation that C60 molecules collect at an air–water interface suggests that a Langmuir trough might be used to prepare and study thin films of C60, perhaps with high levels of molecular ordering.

The preparation of monolayer films of C60 in Langmuir troughs has been attempted by a number of groups, with varying results. Mirkin and Caldwell⁷ have reviewed some of this work. The first studies by Obeng, Bard, and co-workers^{8–10} seemed to indicate that a monolayer could be prepared, but other groups found it difficult to reproduce their results. It now appears that monolayer production is possible only for a very narrow range of experimental conditions.^{10,11} A very dilute solution of C60 in a spreading agent must be used, and macroscopic areas of monolayer are difficult to achieve, with multiple layers forming easily. Crystallites, holes in the film or intricate patterns of single, double, and triple layers may form.^{11–13}

A great deal of experimental effort has gone into attempts to prepare fullerene films using various techniques, but theoretical understanding of the behavior of C60 at the air–water interface has lagged behind experiments. Here, using Langevin equations, we develop a model which accounts for some of the observed behavior, and the model's properties are studied. Using standard methods of statistical mechanics, we estimate the rates of various processes that may occur in the air–water–C60 system. As well as the theoretical methods described here, computer simulations can be used to study the model. Work on this subject is in progress and will be described in a later paper.

The properties of a film of C60 molecules are rather different from those of the films of amphiphilic materials more commonly used in Langmuir troughs. The basic observation that explains this difference is that a C60 molecule is bound weakly to the water surface. This weak binding has several consequences. First, the minimum-energy state of the system is not a monolayer film. Because the van der Waals binding energy between two fullerene molecules is of the same order as the binding energy between a fullerene and water, a three-dimensional lump or "crystallite" of fullerene where each molecule is bound to up

to 12 others has a lower energy than a monolayer film on the water surface. The weak C60–water binding energy also makes possible two events which are rare in Langmuir films of amphiphilic materials. A C60 molecule may escape from the air–water interface completely; or it may move out of direct contact with the water while remaining in contact with other C60 molecules at the interface, thus creating multiple-layer materials rather than monolayers.

As we discuss in section 5.2, despite these processes, a large monolayer film may remain stable for hours because the processes which tend to disrupt its structure occur slowly and only at the edges of the film. Even if defects or holes in the film exist, they do not reduce the stability very much, for reasons which we describe.

2. The Forces on a C60 Molecule at the Air–Water Interface

A potential for the interaction between two C60 molecules has been derived by Girifalco.¹⁴ Because the C60 molecule is rotationally excited at room temperature, the potential is spherically symmetric. Rather than considering the electron distribution in the C60–water system, we treat the water as a continuum and introduce a surface energy γ_C per unit area for the fullerene–water interface. The motion of a C60 molecule near the water surface is then influenced by the balance between the C60–water surface energy and the air–water surface energy (surface tension) Γ_A . Because the fullerene molecule, at 7 Å across, is several times the size of a water molecule (around 2 Å), the error introduced by the continuum approximation should not be large.

We also assume that the air–water interface can be modeled as a sharp discontinuity where water stops and air begins. Because of the short range of the forces which hold liquid water together, the thickness of the surface region in water is not much more than the size of a water molecule, and so this assumption is reasonable.

A third assumption is that the water surface is not deformed from its plane except where it is in immediate contact with a fullerene molecule. At first sight, this assumption does not seem reasonable. It is common experience that a water surface near an area of contact with a solid is not usually flat. However, on the space and time scales of molecular motion on the liquid surface, two factors act to prevent this deformation. The first

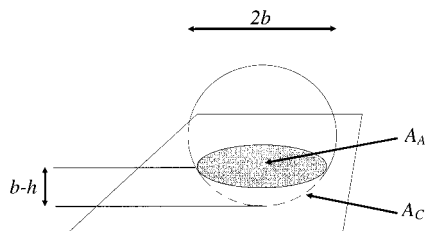


Figure 1. A C60 molecule is modeled as a sphere of radius b sitting in contact with an otherwise flat water surface. The area of contact is A_C , and the area of air–water interface removed by the presence of the sphere is A_A .

is the large effect of viscosity, and the second is the low speed of travel of capillary waves on the liquid surface.

A C60 molecule has a mass of approximately 10^{-24} kg, and so at room temperature has a thermal velocity u of around 100 m s^{-1} . Since the molecule's diameter is 7 \AA , and the viscosity of water is 0.0015 N s , the Reynolds number $R = \rho u l / \eta$ is of order 0.05 . This means that viscous forces dominate over inertial forces, water surface waves are overdamped, and the water behaves on these space and time scales more like treacle than like the liquid we use to make tea. An estimate of the speed of propagation of a disturbance on the liquid surface is given by the group velocity of capillary waves,¹⁵ $v = 3/2(\omega\sigma/\rho)^{1/2}$ for a wave with frequency ω . The size of the region influenced by events generating waves of frequency $\omega = 2\pi/\tau$ on a time scale τ is therefore $r = 3/2(2\pi\sigma\tau^2/\rho)^{1/3}$. Events lasting times of the order of 1 ps therefore interact with the water only in a region of size about 1 nm , or about the size of a C60 molecule. As we shall see, the random interaction between a C60 molecule and the water surrounding it is so strong that the time scales involved in the molecule's motion are shorter than 1 ps . We therefore expect the deformation of the water surface as a molecule moves to be small.

2.1. C60–C60 Interaction. The force between two C60 molecules is described by the potential

$$g(r) = \alpha \left(\frac{1}{s(s-1)^3} + \frac{1}{s(s+1)^3} - \frac{2}{s^4} \right) + \beta \left(\frac{1}{s(s-1)^9} + \frac{1}{s(s+1)^9} - \frac{2}{s^{10}} \right) \quad (1)$$

where $s = r/(2a)$ and a is the C60 radius, 3.55 \AA . The constants α and β have the values 4.677×10^{-2} and $8.485 \times 10^{-5} \text{ eV}$. This potential was obtained by Girifalco¹⁴ by treating the C60 molecule as if it were a sphere with a uniform density of carbon atoms. Theoretical treatments of fullerite crystals based on the Girifalco potential are in excellent agreement with experiment,¹⁶ and the potential has been used in a number of computer simulations.¹⁷ The minimum of this potential is at 1.41 diameters, or 10.06 \AA . The binding energy is $\epsilon_C = 0.277 \text{ eV}$. A graph of the Girifalco potential is included in Figure 2.

2.2. C60–Water Interaction. To model the interaction between a C60 molecule and the water surface, we imagine a C60 molecule as a sphere of radius b sitting in contact with an otherwise horizontal water surface. We take the value of b to be half the equilibrium spacing of two C60 molecules, or 5.03 \AA .¹⁴ This is different from the “radius” $a = 3.55 \text{ \AA}$ of a C60 molecule, which is the distance of the component carbon atoms from the molecule's center.

If the sphere's center is a distance h above the surface, the area of contact between the sphere and the water is

$$A_C = 2\pi b(b-h) \quad (2)$$

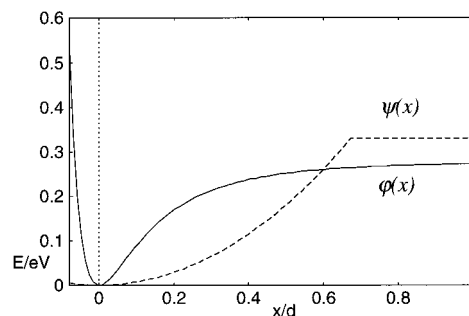


Figure 2. The potential $\psi(x)$ is a model of the interaction between a C60 molecule and the water surface, where x is the height of the molecule above its equilibrium position. The Girifalco potential $\phi(r)$ represents the interaction between two C60 molecules. The minimum of the Girifalco potential, shown at $x = 0$ in this figure, occurs when the centers of two molecules are 10.06 \AA or 1.41 diameters apart. The unit for the horizontal scale is the diameter $d = 7.1 \text{ \AA}$ of a C60 molecule.

as shown in Figure 1. The area of air–water interface removed by the presence of the sphere is

$$A_A = \pi(b^2 - h^2) \quad (3)$$

If the surface free energy per unit area is γ_C for the water–C60 surface and $\Gamma_A = 0.073 \text{ J m}^{-2}$ for the water–air surface, the total free energy is

$$\psi = A_C \gamma_C - A_A \Gamma_A \quad (4)$$

or, neglecting constant terms,

$$\psi(h) = -2\pi b h \gamma_C + \pi h^2 \Gamma_A \quad (5)$$

It is important to note that γ_C is not the macroscopic surface tension between water and a crystal of fullerite, but the interfacial free energy of a unit area of the surface of a C60 molecule in contact with water.

The function $\psi(h)$ has a minimum at

$$h_0 = b \frac{\gamma_C}{\Gamma_A} \quad (6)$$

This determines the equilibrium position of the C60 molecule in the liquid. The force on a molecule when it is displaced from its equilibrium position, but still in contact with the surface, is the negative of the derivative of the potential ψ . Allowing for the fact that the force must be zero when the C60 molecule is not in contact with the liquid surface, we have

$$\psi(z) = \begin{cases} \pi \Gamma_A z^2; & -(b+h_0) < z < b-h_0 \\ \pi \Gamma_A (b+h_0)^2; & z < -(b+h_0) \\ \pi \Gamma_A (b-h_0)^2; & z > b-h_0 \end{cases} \quad (7)$$

where $z = h - h_0$. In other words, the potential is parabolic up to a maximum displacement which is larger when the C60 moves down from equilibrium than when it moves up. For values of z greater than this maximum displacement there is no force.

Figure 2 shows the Girifalco potential and the potential of interaction between a C60 molecule and the water surface. The value of γ_C , which determines the depth of the C60–water potential, has been fixed at the mean value described in the next section. The two potentials have roughly the same binding energy, but the C60–C60 interaction has a much shorter range.

The binding energy between a C60 molecule and the water surface is the energy required to move from the equilibrium position into the air:

$$\epsilon_w = \pi\Gamma_A (b - h_0)^2 = \pi b^2 \Gamma_A \left(1 - \frac{\gamma_C}{\Gamma_A}\right)^2 \quad (8)$$

2.3. The C60–Water Work of Adhesion, Binding Energy and Contact Angle. There is only one unknown parameter in the model described above: the C60–water surface energy γ_C . To estimate the value of γ_C , we must relate it to some measurable quantity. One such quantity is the contact angle between C60 and water, which has been measured by Obeng and Bard⁹ and by Tronel–Peyroz et al.¹⁸ In this section, we derive the relationship between γ_C and the contact angle, and also relate the contact angle to the water–C60 binding energy ϵ_w .

The relationship between the contact angle and the work of adhesion w is given by the Young–Dupré equation¹⁹

$$w = \Gamma_A (1 + \cos \theta) \quad (9)$$

We assume that C60 molecules at the interface are arranged in a triangular lattice with nearest-neighbor distance $D = 2b = 10.06 \text{ \AA}$.¹⁴ The area per molecule is then $\alpha = D^2\sqrt{3}/2$, and the work of adhesion is

$$w = \frac{\epsilon_w}{\alpha} \quad (10)$$

We can therefore calculate the water–C60 binding energy ϵ_w from the contact angle:

$$\epsilon_w = \alpha\Gamma_A (1 + \cos \theta) \quad (11)$$

It is important to note that this value of the binding energy does not depend on the details of the model described in section 2. The only assumption required is that C60 molecules interact individually with the water surface and that the measured contact angle relates directly to the surface energy via the Young–Dupré equation. Measurements of contact angles are known to be unreliable.¹⁹ However, in the absence of other data relating to the C60–water interaction, this is the best available estimate of ϵ_w .

The values of the contact angle θ measured by Obeng and Bard⁹ and by Tronel–Peyroz et al.¹⁸ are 110° and 100° , respectively. The corresponding values of ϵ_w given by eq 11 are 0.263 and 0.330 eV. In the calculations below, we use $\epsilon_w = 0.3 \text{ eV}$ as an estimate of the binding energy. The uncertainty of around 20% in this value causes estimates of rates to be uncertain by a factor of four, as one might expect from a Boltzmann factor $e^{\epsilon_w/KT}$.

The binding energy ϵ_w is related to the C60–water surface energy γ_C by eq 8, so we can also determine γ_C . For $\epsilon_w = 0.3 \text{ eV}$, we obtain $\gamma_C/\Gamma_A = 0.09$. The ratio $\gamma_C/\Gamma_A = h_0/b$, so the equilibrium height of the center of a C60 molecule above the water surface is about one-tenth of its radius.

An independent estimate of the order of magnitude of the C60–water interaction can be found using an approach first suggested by Girifalco and Good²⁰ and modified by Fowkes,²¹ and based on the idea that the dispersion interaction between molecules of two different types should be approximately equal to the geometric mean of the self-interactions. Fowkes' equation for the work of adhesion between water and some other substance C is

$$w = 2 (\gamma_w^d \gamma_C)^{1/2} \quad (12)$$

where γ_C is the surface tension of C and γ_w^d is the component of the water surface tension due to dispersion forces, estimated by Fowkes as 0.0218 J m^{-2} . Using this equation with the value $\gamma_C = 0.058 \text{ J m}^{-2}$ estimated by Girifalco,¹⁴ we obtain $w = 0.0711 \text{ J m}^{-2}$, and so $\epsilon_w = 0.39 \text{ eV}$. This figure is rather larger than the estimates from contact angle measurements, but the author is inclined to treat it with some skepticism because of the unusual nature of the fullerene molecule, for which the Girifalco–Good–Fowkes method is untested. Use of this figure in place of those from contact angle measurements would alter the rates and times calculated in this paper by an order of magnitude, but would leave the general conclusions unchanged.

2.4. Viscous Forces. An approximate value for the viscous drag force on the molecule can be obtained from Stokes' formula for the drag on a sphere of radius b moving with velocity v in a viscous fluid. The work of Brey and Ordóñez²² suggests that the no-slip boundary condition is appropriate, so that the drag force on a sphere is $F = -4\pi b\eta v$. For the vertical motion of the molecule we use this equation, whereas for the horizontal motion we use $F = -2\pi b\eta v$, because only about one-half of the sphere is immersed.

2.5. Molecular Fluctuations. We model the effect of thermal noise on the dynamics of a C60 molecule using a Langevin equation.²³ That is, we add a temporally uncorrelated random force to the equation of motion, setting its magnitude so that the equipartition theorem is satisfied. In general, for a body of mass M , acted upon by a frictional force $-\gamma Mv$ and a conservative force f , we use an equation of motion

$$M \frac{dv}{dt} + \gamma Mv = f + (2\gamma MKT)^{1/2} n(t) \quad (13)$$

where $n(t)$ is a Gaussian stochastic process defined by the ensemble averages

$$\langle n(t) \rangle = 0 \quad (14)$$

and

$$\langle n(t)n(t') \rangle = \delta(t - t') \quad (15)$$

The process $n(t)$ is often referred to as “white Gaussian noise”.

There is one Langevin equation for each degree of translational freedom in the motion of a C60 molecule. For horizontal motion, $\gamma = 2\pi b\eta/M$, and for vertical motion, $\gamma = 4\pi b\eta/M$, as discussed above. The forces f are those calculated from the Girifalco potential for interaction between C60 molecules and (for vertical motion) the surface force between a C60 molecule and water. Both the frictional force and the random force stem from coupling between a C60 molecule and water, so they are both absent when the molecule loses contact with the water surface.

3. Rates of Escape Processes

Many of the processes that occur in collections of C60 molecules at a water–air interface involve the escape of a molecule from a potential well. These processes include the escape of a C60 from the surface, separation of a molecule from a raft, and rearrangement of the structure of a raft. In this section, we estimate two escape rates which are important for the behavior of fullerene films: the rate for the separation of two C60 molecules and the rate for the escape of a lone molecule from the water surface.

3.1. Diffusive and Ballistic Motion. Before studying the kinetics of these processes in more detail, we must distinguish between processes that occur when a C60 molecule is in direct contact with the water and processes in which the molecule is in contact only with other C60 molecules, which themselves may be in contact with water. The difference is important because in the first case, the motion of a C60 molecule is diffusive, whereas in the second case, it is ballistic. In other words, when a molecule is in contact with water, the frictional force and the random force are strong compared to the conservative forces (from the C60–C60 and the C60–water interaction), and the molecule executes Brownian motion with a long-term drift influenced by the conservative forces. When the molecule is not in contact with the liquid, there is no friction and the molecule oscillates in its potential well, with jostling from other C60 molecules perturbing the motion.

To justify this conclusion, we calculate some time scales for the C60–water system. The viscous damping time for a C60 molecule in contact with water is at most

$$\tau_\eta = \frac{1}{\gamma} = \frac{M}{4\pi\gamma b} = 0.25 \text{ ps} \quad (16)$$

The time τ_η is also a typical time scale for fluctuations. The shortness of this time justifies the assertion made earlier that the interaction of a C60 molecule with the water surface is local. Oscillation times for the C60–water and the C60–C60 potentials can be calculated by approximating the potentials as $M\omega^2 x^2/2$ near their minima, giving for the C60–water bond a frequency

$$\omega_A^2 = \frac{2\pi\Gamma_A}{M} \quad (17)$$

and an oscillation period $\tau = 2\pi/\omega \approx 10$ ps. For the C60–C60 bond, from the second derivative of the potential at its minimum we have $\omega = 3.7 \times 10^{12} \text{ s}^{-1}$ and $\tau \approx 2$ ps. Because the time scales of motion under the conservative forces are much longer than the damping time, when a C60 molecule is in contact with water its motion is diffusive.

3.2. Escape from the Water Surface. Until a C60 molecule has escaped from the water surface, its motion is diffusive. We therefore use an equation derived by Chandrasekhar²³ and earlier by Smoluchowski, for the rate $P = 1/\tau_d$ of escape. In the notation used here, the equation reads

$$\tau_d = \frac{\gamma}{\omega_A} \left(\frac{2\pi M}{kT} \right)^{1/2} \int_A^B e^{\phi(x)/kT} dx \quad (18)$$

where γ is the strength of damping, ω_A is the natural frequency of small oscillations around the potential's minimum, A is the point where the potential has a minimum and B is a point in the region to which the particle may escape.

The parameter γ for vertical motion is $4\pi\eta b/M$, and the natural frequency of the water–C60 bond is given by equation 17. Choosing B to be the point at which contact is lost, and using the surface interaction potential ψ , we obtain

$$\tau_b = \frac{4\pi\eta b\sqrt{\pi}}{\Gamma_A} \int_0^L e^{\psi} dt \quad (19)$$

where the upper limit of the integral is

$$L = \left(\frac{\pi\Gamma_A}{kT} \right)^{1/2} (b - h_0) \quad (20)$$

For $\epsilon_W = 0.3 \text{ eV}$, the value of L is 3.44 and numerical integration yields the value 21 000 for the integral. The escape time is therefore $1.5 \mu\text{s}$. The larger and smaller values of ϵ_W implied by the measurements of Tronel–Peyroz et al. and Obeng and Bard give escape times of 4.8 and $0.4 \mu\text{s}$, respectively.

3.3. Ballistic Escape from the C60–C60 Bond. Another physically relevant process is one in which a C60–C60 bond must be broken in order to rearrange the structure of a “raft” of molecules on the surface. Because one or both of the molecules will be out of contact with the water surface in this case, we use the formula for escape in the ballistic case.^{23,24} When the escape is slow, the rate of escape is independent of the shape of the potential curve near the maximum and of the damping, and is as given by the transition-state approximation.²⁴ The escape time is

$$\tau_b = \frac{2\pi}{\omega_A} e^{E/kT} \quad (21)$$

where E is the height of the potential barrier and ω_A describes the shape of the potential near the minimum. The result of applying this formula to the Girifalco potential is an escape time of $0.1 \mu\text{s}$.

3.4. Other Processes. We can draw some conclusions about the rates of processes where multiple bonds are broken by the same methods. Any process that requires more than one C60–C60 bond to be broken will occur very slowly, because the escape time will be larger than the corresponding escape time from a single bond by a Boltzmann factor $e^{\epsilon/kT} \sim 60\,000$ for each additional bond. The breaking of an additional C60–water bond multiplies the escape time by a similar factor. For two molecules at the air–water interface, the time for escape from the surface is therefore around 0.2 s, and for three molecules, the time is 6 h.

4. Two-Dimensional Gas Phase

A C60 molecule attached to the water surface but to no other C60 molecules is in a two-dimensional gas phase. There are two ways in which the molecule can move from this phase into another. The molecule may escape from the water surface, or it may attach itself to other C60 molecules, forming part of a “raft” of molecules in a condensed two-dimensional phase.

The correlation time for fluctuations of the horizontal component of the velocity of a single C60 molecule is less than 1 ps (see section 2.5). Over time scales longer than this, the motion is diffusive: paths followed by C60 molecules are like those of a Brownian particle. The one-dimensional gas phase is therefore very different from an ideal gas of free particles. The diffusion coefficient for horizontal motion can be calculated from the Langevin equations of section 2.5 (See Chandrasekhar²³ or Feynman,²⁵ section 41). It is

$$D = \frac{kT}{M\gamma} \approx 9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \quad (22)$$

The mean distance travelled by a C60 molecule on the surface in a time t is $(4Dt)^{1/2}$. In the escape time of around $1.5 \mu\text{s}$, a molecule travels only about 70 nm. If a region of “gas phase” surrounded by a condensed phase is larger than this size, we would expect more molecules to leave it by escaping from the liquid surface than by reaching the boundary. The one-dimensional pressure measured will therefore be much lower than the value given by the ideal gas law.

This observation explains why the pressure exerted by the two-dimensional gas phase has not been measured in experi-

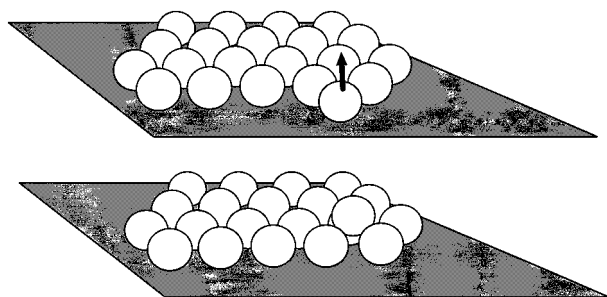


Figure 3. A C60 molecule attached to only two others at the edge of a monolayer raft may move up onto the second layer by a process in which only the C60–water bond is broken.

ments. It also implies that the “foot” of measured two-dimensional pressure–area curves, where the line pressure increases smoothly from a value close to zero,^{10,26} must be due to the early stages of compression of a condensed phase rather than to a two-dimensional gas phase.

5. Structure and Evolution of Films of C60

The interpretation of experimental results on the behavior of films of C60 is controversial,⁷ but it is clear that the minimum-energy state of a single near-spherical fullerite crystal surrounded by almost clean water is not achieved. Any theory of the behavior of the system must therefore rely on kinetics rather than thermodynamics. We must ask which metastable state the system may reach in experiments. In this section, we attempt to answer this question with some simple calculations based on the escape times derived above. We first consider the process of promotion, where a molecule in a monolayer raft may move up onto a second layer, and estimate how quickly this process will decrease the area of a large monolayer once it has formed. We then analyze the first stage of the experiment, where fullerene molecules are deposited on the water surface by evaporation from a solvent and then form clusters. The discussion is arranged in this apparently perverse order because some information about the rate of promotion is useful when the clustering process is considered.

5.1. Promotion of Monolayer Molecules to a Second Layer. A monomolecular layer of C60 molecules at the air–water interface may be stable if its structure is sufficiently regular. If every C60 is attached to six neighbors, the elevation of a C60 to a second layer must involve diffusive breaking of at least two C60–C60 bonds as well as the C60–water bond, a process with a time scale of at least a few minutes.

The stability of a monolayer is removed by the presence of edges. These allow the creation of a second layer, by the process where a C60 molecule on the edge of the monolayer raft leaves the water surface and is promoted to the second layer. In the case where the promoted molecule is initially in contact with only two others, no C60–C60 bond is broken and the process is essentially a diffusive escape from the water surface, and therefore takes around 1.5 μ s on average. This process is illustrated in Figure 3.

For any edge of a hexagonal lattice of molecules at the water–air interface, molecules in contact with only two others will quickly be removed to the second layer by this process. The edge will then consist entirely of molecules in contact with three, four, or five neighbors. Promotion for these molecules is much slower, because it involves the breaking of a C60–C60 bond as well as a C60–water bond. According to the argument given in section 3.4, the promotion of a C60 molecule with three neighbors should take about 60 000 times longer than the diffusive breaking of the C60–water bond, or around 0.1 s.

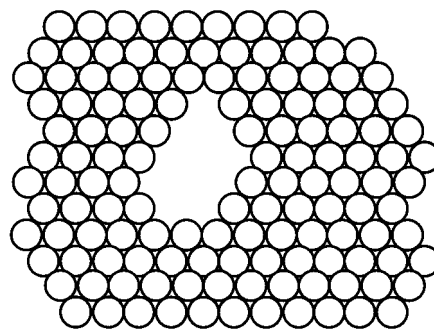


Figure 4. A hole in an infinite monolayer may have a shape where no molecule has fewer than four neighbors. However, an “island” of monolayer surrounded by water surface must always have some molecules with three or fewer neighbors.

After molecules are promoted to the second layer in this way, they may move by a hopping diffusion process where a single C60–C60 bond is broken in each hop. The time scale for a hop is therefore the time calculated in section 3.3, about 0.1 μ s. Because this is much shorter than the time for promotion, we expect the molecules of the second layer to escape from the boundary area of a hole much more quickly than they are produced. This makes it unlikely that a molecule will meet another second-layer molecule immediately after it is promoted.

5.2. Evolution of the Shape of Monolayer Rafts. At the edge of any monolayer raft, the promotion process will cause a slow decrease in area as molecules move into the second layer. As can be seen from Figure 4, it is possible for a hole in an infinite monolayer to have a shape where no molecule has fewer than four neighbors. However, an “island” of monolayer surrounded by water surface must always have some molecules with three or fewer neighbors. We might therefore expect to see holes which are stable in a monolayer raft while the raft shrinks by promotion of molecules at its outer edges. To estimate the speed of this shrinkage, we need to know the fraction of edge molecules that have three neighbors. More precisely, we define the edge fraction f as the ratio of the number of molecules with fewer than six neighbors to the total number of molecules. It is not obvious how to estimate f theoretically, so a simple computer simulation has been carried out.

In the simulation, sites on a large (10^5 sites) hexagonal lattice are either occupied by a first-layer molecule or unoccupied. Time proceeds in discrete steps, and at each time step, every molecule with fewer than three neighbors is removed from the lattice and the probability that each molecule with exactly three neighbors will be removed is p . The program thus mimics the promotion of molecules from a monolayer that is a single two-dimensional crystal, ignoring the influence of molecules after they have been promoted to the second layer. A real monolayer is unlikely to be a single crystal, but defects in the crystal structure will cause a small decrease in the average number of nearest neighbors and so increase the rate of promotion by a small amount.

For a variety of starting configurations that contain simply connected domains of monolayer, and for values of p smaller than around 0.1, the simulations show convergence towards $f \approx 0.2$. Figure 5 shows an example of a starting configuration and the result of running the simulation for 200 steps, and also the evolution of the fraction f over the course of the simulation.

The results of the simulations suggest that a monolayer raft will decrease in surface area at a rate of about $f = 0.2$ times the rate that would occur if all edge molecules had exactly three neighbors. Since the time for promotion of a molecule with

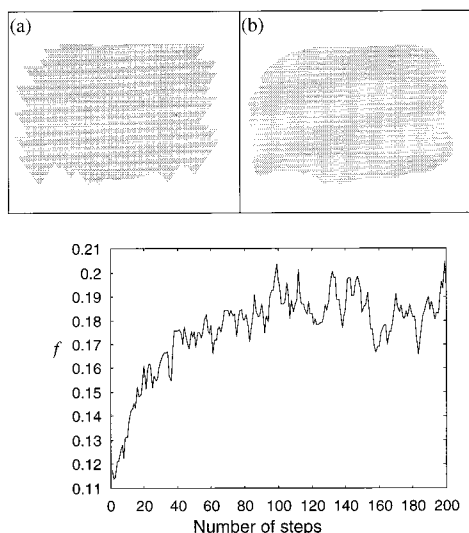


Figure 5. (a) shows the starting configuration, and (b) the configuration after 200 steps, of a monolayer raft where promotion of molecules is simulated as described in the text with $p = 0.05$. The graph shows the evolution of the fraction f of edge molecules having exactly three neighbors.

three neighbors is around 0.1 s, we expect the average time for an edge molecule to be promoted to be of the order of 1 s. This means that the edge of a monolayer raft should move at a rate of about one molecular spacing per second, or 1 nm s^{-1} . In a few minutes, the edge would move by a distance of a micron. This process might therefore be observed using careful optical microscopy.

6. Evaporation and Clustering in the First Stage of an Experiment

The most common experimental procedure^{8–13} is to spread a dilute solution of C60 in benzene over the water surface of a Langmuir trough, allow the benzene to evaporate for up to half an hour, and then begin to compress the surface. As Bulhøes et al.¹⁰ have noted, it is important that, before evaporation, the C60–benzene solution can spread far enough so that the surface density of C60 is less than for a monolayer. If evaporation occurs with a surface density greater than that for a monolayer, multiple layers will form.

If the surface coverage is low enough so that nearly all C60 molecules are at first placed in contact with the water surface by evaporation, then the final structure of the film is determined by competition between two processes: the clustering of C60 molecules to form monolayer rafts, and the promotion of molecules at the edges of these rafts to form multiple layers. Some molecules will also leave the surface completely by thermal excitation, but since these are effectively removed we can ignore them. To determine which process “wins” the competition between clustering and promotion, we must estimate whether a molecule at the edge of a monolayer raft is more likely to be promoted or to be surrounded by other molecules attaching themselves to the edge.

As we saw in section 5.1, the time for promotion of an edge molecule is approximately 0.5 s in a large monolayer raft. In the early stages of aggregation the average number of neighbors will be smaller than in a large raft, but in any case the time for promotion cannot be smaller than the time for an isolated molecule to leave the surface, or about $0.5 \mu\text{s}$.

A very rough estimate of the rate of aggregation will be sufficient to make a comparison. The two-dimensional “gas”

of C60 molecules that have not yet clustered is not an ideal gas in the normal sense because of the large interaction with the water. However, in the case where the C60 molecules are far enough separated so that their interactions can be ignored, the distributions of positions and velocities are the same as those for an ideal gas, and so the rate of collisions with the walls of the container or the edge of a growing monolayer raft are the same as for an ideal gas. The rate of collision per unit length is of the same order as the rms velocity $\bar{v} = (kT/M)^{1/2}$ multiplied by the number density $n = 1/A$ where A is the area per molecule. The mean time we should have to wait for a C60 molecule from the gas to strike a length $D = 10 \text{ Å}$ of edge is therefore

$$\tau_a \sim \frac{A}{\bar{v}D} = \frac{D\sqrt{3}A}{2\bar{v}\alpha} \quad (23)$$

where α is the area per molecule in a monolayer (see section 2.3). Because the rms velocity is around 100 m s^{-1} , we have

$$\tau_a \sim \frac{A}{\alpha} \times 10^{-11} \text{ s} \quad (24)$$

Even when the area per molecule A is 20 times greater than the monolayer value α , as in some experiments,¹⁰ the aggregation time τ_a is less than a nanosecond, so any edge molecule can expect to gain neighbors more than one thousand times faster than it is promoted. This means that we should expect the process of evaporation and aggregation to yield a film which is predominantly a monolayer.

7. Conclusion

The model of the water–air–C60 system described here is approximate, but captures the essential physics of the system. The escape times should be considered estimates of the order of magnitude rather than precise figures, but the physical conclusions reached depend only on these orders of magnitude, and not on the precise values of the rates.

The results described here give us some insight into the results of experiments with C60 molecules at the air–water interface. The interpretation of experimental results has been controversial since Obeng, Bard, and their co-workers^{8–10} found that the formation of monolayers was possible. Other groups^{12,26–28} have found multilayer films, with the C60 film showing resistance to compression only when a surface coverage more than three times greater than that of a monolayer is reached.

The discussion presented in this paper suggests that a monolayer should indeed be the result of an experiment carried out in a clean and carefully controlled environment. However, because the monolayer is not the equilibrium state of the system, any influence that disturbs the experiment will tend to lead to the formation of multiple layers. For example, any vibrations will cause capillary waves on the water surface; these will disrupt the monolayer and allow folding of the film or promotion of molecules to the second layer.

The picture of a fullerene film that emerges from these calculations has several interesting features which make it different from the more conventional films of amphiphilic materials. All these features stem from the relatively low binding energy of a fullerene molecule to the water surface. The short escape time of a single C60 molecule from the surface means that the two-dimensional gas phase does not exist in practice. It appears that C60 does not possess a stable liquid phase, either in two or in three dimensions.¹³ The only phases available to a C60 film are therefore solid, perhaps with gaps. But there is a variety of solid states. The possibility of double

and multiple-layer stacking of molecules at the surface, even when a low external pressure is applied, allows the formation of complex structures of holes and islands of monolayer and multiple-layer films.

The results of this paper suggest a number of possible experiments. It should be possible to observe with an optical microscope the early stages of clustering in a monolayer, and the reduction in area of monolayer rafts by the promotion of molecules to the second layer. Brewster angle microscopy of the "monolayer" films prepared by Obeng, Bard, and their co-workers might show that these films are not homogeneous in structure, but have many holes and perhaps areas of multiple layers produced by the promotion mechanism. Optical microscopy could also be used to observe the Brownian motion of a small cluster of fullerene molecules at the surface, yielding information about the coupling of the fullerenes to the liquid.

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