

The Effect of Inhibition of Molecular Reorientation and the Resulting Consequences for the Dilatational Elastic Modulus[†]

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Surface light scattering investigations of the propagation of thermally excited capillary waves on the surface of a surfactant solution (triisopropylphosphine oxide) have been carried out. The surfactant had a specifically designed geometry, to eliminate the possibility of molecular reorientation in the absorption layer. The absence of such motions are demonstrated by the absence of any deviation in the dilatational elastic modulus from the value calculated from the equilibrium surface tension versus concentration isotherm, at concentrations appropriate to reorientation in ordinary surfactant adsorption layers.

1. Introduction

Some time ago, to find a more general solution for describing soluble amphiphiles' equilibrium surface tension (σ_e) vs concentration (c) isotherms by a surface equation of state covering the entire concentration region satisfactorily, the so-called "two state" approach^{1,2} was proposed. This implied that an extended chain amphiphile is assumed to adsorb flat at very low surface coverages, but somehow upright near surface saturation. The transition from one to the other alternative surface configuration is assumed, not to occur as an all-or-nothing phase transition at a certain concentration, but rather within an interval of certain width at medium concentrations. For convenience the "transitional interval" was assumed to contain a mixture of (at least two) alternative surface configurations. However, it is also imaginable that the surface transitional region consists of amphiphiles adsorbed in different conformations such as those suggested by Vold³ and recently by Warszynski et al.⁴

Although this approach represents a reasonable thermodynamic hypothesis, which so far has been applied successfully, e.g., leading to the discovery of hitherto unknown adsorption properties such as phenomena of alternation and changes of cross-sectional area within homologous series,^{5–8} we endeavored to learn more about the physical properties of the adsorption layers' transitional region, if it does indeed exist. Hence additional support was looked for from some surface investigations other than thermodynamic, i.e., from surface rheological and electric experiments.

The surface dilatational elastic modulus, measured by light scattering from thermally excited capillary waves of frequency

between $5 \times 10^4 \text{ s}^{-1}$ and $9 \times 10^5 \text{ s}^{-1}$ for two different n -alkyl amphiphiles, agreed with the equilibrium value derived from the equilibrium surface pressure– $\ln c$ variation for concentrations, below and above, the transitional region. However, it systematically exceeded the equilibrium variation between these concentrations, i.e., within this region. Therefore, surface light scattering is extremely convenient for the investigation of this transitional region, due to its sensitivity to the dilatational surface properties, particularly at those surface pressures which cover the transitional region.^{9,10} The unique behavior of the elastic modulus can be explained by relaxation involving molecular reorientation within the adsorbed layer, with a relaxation time $\gg 4 \text{ } \mu\text{s}$.^{11–13}

Thus, having previously found some evidence for reorientation of the adsorbed surfactant molecules in the adsorption layers' transitional region from surface light scattering investigations, it seemed logical to provide further support by investigating amphiphile molecules which are prevented from adopting different surface configurations due to their particular molecular structure. In addition, this would support the validity of the interpretation of the deviation of the dilatational elastic modulus values.

It was decided to link bulky hydrophobic substituents to a hydrophilic headgroup (Figure 1) like the most bulky configuration of a n -propyl residue, i.e., isopropyl. Now, if three of these hydrophobic residues are linked to the hydrophilic phosphor oxide group, a symmetrical amphiphilic structure results. This is characterized by a rather large cross-sectional area as compared with typical n -alkyl chain amphiphiles, such as n -alkanols, n -alkanoic acids, and n -alkyldimethylphosphine oxides.⁸ If this amphiphile, triisopropylphosphine oxide $\{(\text{i-prop})_3\text{PO}\}$, adsorbs at a fluid interface, it will adopt a config-

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[†] Dedicated to the memory of J. C. Earnshaw.

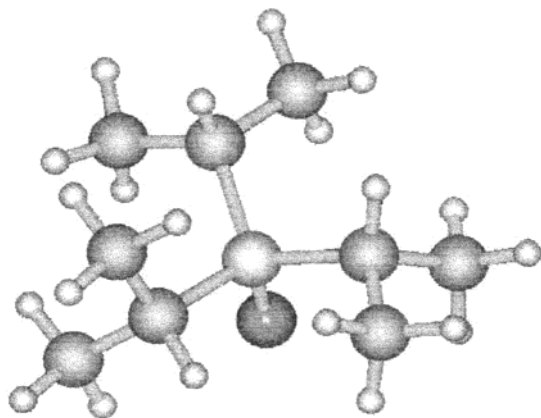


Figure 1. A schematic of the amphiphilic molecule triisopropylphosphine oxide ((i-prop)₃PO).

uration with the polar $-\text{PO}$ group remaining in water, and the hydrophobic, branched, isopropyl groups stretched toward the air phase. Thus, the molecular surface configuration greatly resembles the picture of a parasol.

It is impossible to increase the molecules' girth at the expense of their chain length by adopting irregular conformations via rotation of the isopropyl, or methyl, groups about the $\text{C}-\text{C}$ bonds. Therefore, if there is a characteristic "transitional behavior" found for n -alkyl chain amphiphiles due to the possibility of adopting various surface conformations, then this behavior ought not to occur for this particular amphiphile ((i-prop)₃PO). This becomes obvious from simple stereogeometrical considerations.

2. Background

A liquid surface is never flat due to the influence of thermal fluctuations (amplitude ~ 2 Å) which create various types of waves on this surface. A number of modes^{14,15} may be sustained of which two are significant here: capillary and dilatational waves. The former are subject to the surface tension σ , and the latter to the dilatational elastic modulus ϵ .

The frequency and wavenumber are related through the surface wave dispersion equation^{9,16} to the physical properties of the system. In the presence of a monolayer on the liquid surface there may be dissipative processes. These can be incorporated in the formalism by expanding σ and ϵ as linear response functions:¹⁷

$$\begin{aligned}\sigma &= \sigma_0 + i\omega\sigma' \\ \epsilon &= \epsilon_0 + i\omega\epsilon'\end{aligned}\quad (1)$$

where σ' is the transverse shear viscosity and ϵ' the dilatational viscosity. For any surface that exhibits viscoelastic behavior, these properties may be frequency dependent.

There are two roots to the dispersion equation, corresponding to the capillary and dilatational waves, ω_C and ω_D , respectively.¹⁸ At low wavenumber, q , both modes propagate as damped oscillators, and both become overdamped at a (different) critical q . To first order these can be approximated as

$$\begin{aligned}\omega_C &\approx \left(\frac{\sigma q^3}{\rho}\right)^{1/2} + i\left(\frac{2\eta q^2}{\rho}\right) \\ \omega_D &\approx \left(\frac{1}{2}\right)(\sqrt{3} + i)\left(\frac{\epsilon^2 q^4}{\eta\rho}\right)^{1/3}\end{aligned}\quad (2)$$

where η and ρ are the fluid viscosity and density. Surface light

scattering probes the capillary waves only, since the intensity of light scattered by the dilatational waves is several orders of magnitude lower than for the capillary waves. Since the two modes are coupled¹⁹ at the liquid surface, we know the dilatational surface properties will affect the capillary waves.

3. Experimental Section

3.1. Surface Tension Measurement. The surface tension was determined at 22 °C using a Lauda ring tensiometer, taking into account the modifications necessary when this method is applied to surfactant solutions.²⁰

3.2. Purification. To obtain reliable surface tension data it is important to ensure that the purity of the surfactant solutions is of a sufficiently high value. Since surfactants used "as received" will never fulfill this requirement, stock solutions were purified by an automated high-performance purification apparatus.²¹ The state of "surface-chemical" purity was checked by applying the criterion proposed by one of us previously.²²

3.3. Light Scattering. The setup has been described in depth previously,²³ and a brief summary is given below. Light from an Ar^+ ion laser, at a wavelength of 488 nm, was incident on the liquid surface. The light was scattered by the capillary waves of different wavenumber values at different angles. To enable the small frequency shifts caused by the capillary waves to be determined, a technique known as heterodyne detection was used. The scattered light was mixed with a reference beam of light at the original laser frequency. By using photon correlation, the temporal evolution of the scattered light was measured and rapid data acquisition²⁴ ensured low noise. A wide q range was investigated, $275 \leq q \leq 1400 \text{ cm}^{-1}$.

The correlation functions obtained can be fitted to give unbiased estimates²⁵ for the values of the capillary wave frequency, ω_0 , and damping, Γ . An alternative direct analysis²⁶ yielded values of the surface properties directly from the correlation functions. For the second analysis initially no constraints were applied, however limiting both σ' and ϵ_0 to be positive improved the reliability of the fitted parameters.

3.4 Material. The material was prepared^{27,28} by dissolving 2 mL of triisopropylphosphine (Aldrich) in 20 mL of diethyl ether, and this was treated with 0.5 g of powdered potassium iodide. Under powerful stirring with cooling and using a reflux condenser, ca. 2 mL of 30% H_2O_2 was added very carefully. The end of the reaction was indicated by the color of iodine in the water phase, which does not disappear if more hydrogen peroxide is added. The water phase was separated from the organic phase and treated with solid NaOH . The formed oil was separated and distilled on a short-path distillation apparatus under reduced pressure, yielding the colorless liquid of triisopropylphosphine oxide (boiling point 126–130 °C at 12 mmHg). The obtained data correspond very well to those given previously.

4. Results

The wave frequency and damping constants are plotted for the highest and lowest concentrations of triisopropylphosphine oxide against the range of wavenumbers investigated (Figure 2). The lines on the graph are the variations for the clean surface of water. The variation of the frequency with concentration is reflecting the change in value of the surface tension. The damping values also increase as would be expected for increasing concentration of surfactant. For the low concentration data, the frequency values are very similar to the pure water values, but the damping values are just higher than those of water. In the case of the higher concentration, the frequencies are smaller

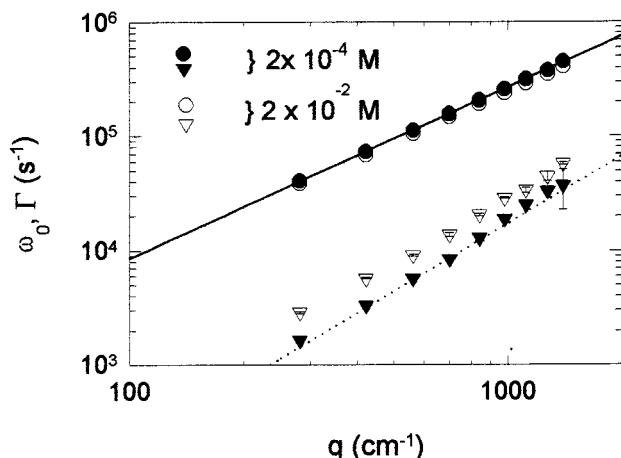


Figure 2. Variation of frequency (ω_0) and damping (Γ) with q . Water frequency (—) and damping (···) values are compared with those at concentrations of 2×10^{-4} M and 2×10^{-2} M triisopropylphosphine oxide.

and the damping noticeably higher, almost double the water value at the larger damping values. Note also the gradients of these lines, the frequency gradient of 1.5 ($\omega_0 \propto q^{3/2}$) and damping gradient of 2 ($\Gamma \propto q^2$) in accord with eq 2.

As mentioned in the Introduction, the expectation that the triisopropylphosphine oxide molecule cannot adopt different surface conformations due to the bulky structure of its hydrophobic substituents is in line with thermodynamic findings. Any hint of change in this bulky amphiphile's surface conformations was not observed, i.e., its σ_e vs c isotherm can be matched ideally by a simple Szyszkowski/Langmuir equation (eq 3),

$$\Delta\sigma_e = RT\Gamma_\infty \ln\left(1 + \frac{c}{a_L}\right) \quad (3a)$$

$$\Gamma = \Gamma_\infty \frac{c}{a_L + c} \quad (3b)$$

within the entire concentration range 1×10^{-4} M $\leq c \leq 2 \times 10^{-1}$ M. This corresponds with $72.2 \text{ mNm}^{-1} \leq \sigma_e \leq 52.0 \text{ mNm}^{-1}$ and a standard deviation of $\pm 0.1 \text{ mNm}^{-1}$. $\Delta\sigma_e$, Γ_∞ , and a_L represent equilibrium surface pressure, saturation adsorption, and surface activity parameter, respectively. The σ_e vs c isotherm is presented in Figure 3.

The adsorption parameters of the best-fit approximation are saturation adsorption, $\Gamma_\infty = 1.98 \times 10^{-10} \text{ mol cm}^{-2}$, and surface activity parameter, $a_L = 3.18 \times 10^{-3} \text{ mol cm}^{-3}$. So the σ_e vs c isotherm possesses ideal surface behavior.²⁹ This corresponds to a cross sectional area of 83.9 \AA^2 per molecule. This value is large in comparison with typical values for n -alkyl surfactants of around $20\text{--}40 \text{ \AA}^2$ per molecule indicating the bulky nature of this molecule.

Figure 3 also contains the surface tension values measured with the surface laser light scattering technique. There is a good agreement between the data obtained with the ring method and the SLLS method. In addition, it should be emphasized that the agreement between these series of measurements was achieved with two quite different techniques, in two separate laboratories, and with a time lapse of about 2 years. This confirmed the stability of the triisopropylphosphine oxide solutions, and together with their ideal surface behavior makes them an ideal amphiphile structure for modeling surface behavior.

The transverse shear viscosity is still not clearly understood³⁰ and some have questioned its existence.³¹ If it indeed exists it

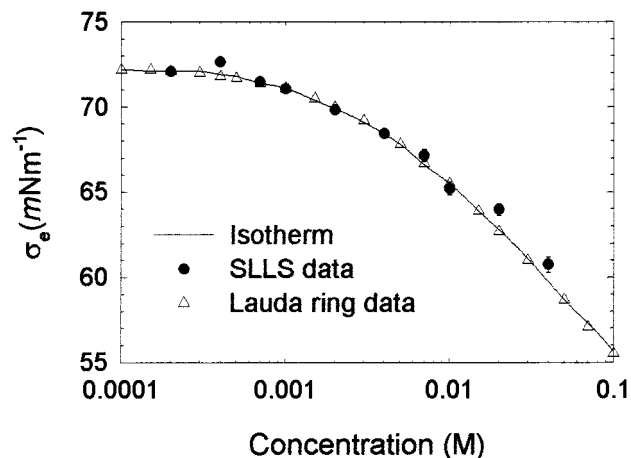


Figure 3. Values of equilibrium surface tension versus concentration isotherm of aqueous solutions of triisopropylphosphine oxide compared to the SLLS data and the Lauda ring data. Here, and elsewhere, where not shown, uncertainties are smaller than the plotted points.

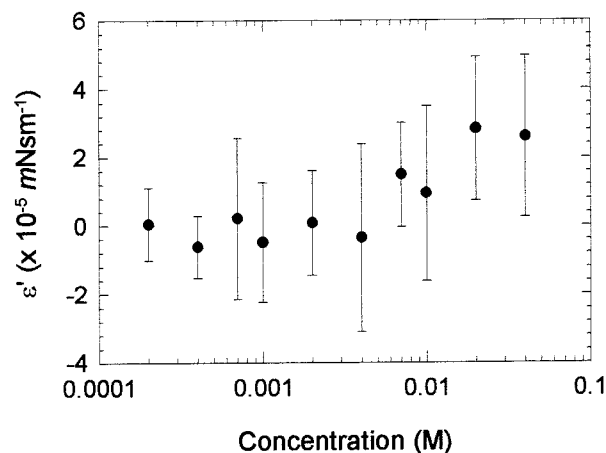


Figure 4. Dilatational viscosity for aqueous solutions of triisopropylphosphine oxide as a function of concentration.

would be expected to be small and detectable at rather high deformation frequencies only. In light of these arguments, a further change to improve the reliability of the direct data analysis involved constraining σ' to be zero. The results showed no change in the parameters except for a slight increase in ϵ_0 , so σ' is taken to be zero. However, this amphiphile with ideal surface behavior, is not convenient for debate on this question. As the main concern of this work was the dilatational elastic modulus, this problem need not be discussed further to avoid speculation. The dilatational viscosities were also averaged and plotted (Figure 4). Before averaging, the values fluctuated randomly with q about zero, as was found previously for nonionic surfactants.³² The values can be seen to be zero for all but the two higher concentrations, which agreed with our finding on re-analyzing the data constraining the dilatational viscosity to be zero. This found there was no change in the values of the other parameters except at the two higher concentrations, implying the dilatational viscosity is nonzero at these concentrations.

5. Discussion

The goal of this investigation was to falsify the effects of reorientation in adsorption layers by choosing an amphiphilic structure that was incapable of adopting different surface configurations and/or conformations due to its particular bulky structure. The effects of reorientation were found previously

for extended *n*-alkyl chain surfactants^{11–13} in the “transitional region”. Here, either different surface configurations (mixtures of flat and upright extended chain configurations) or different surface conformations (conformers with their hydrocarbon chain deviating from the straight chain structure) of the adsorbed molecule were assumed to exist.

The transitional region, for geometrical reasons, sets in at rather low surface pressures when the adsorbed extended chain surfactant molecule starts to become disturbed in its free 2D-rotations in the surface.^{1,2,11–13} It ends when the surface density becomes so high that the cross sectional area per molecule available is too small to accommodate any flat molecule within the adsorption layer, confirming its inability to exist in conformations other than extended chain. The various surface configurations or irregular conformations are discriminated by energy differences. The adopting of different orientations is accompanied by certain, characteristic relaxation times. So, provided reorientation is a real feature of adsorption and provided it can be followed by some physical property, it should be encountered at concentrations within the “transitional region”.

In coincidence with these assumptions, it was found previously that the surface dilatational elastic moduli determined experimentally from laser light scattering experiments deviated considerably from the corresponding values calculated from the equilibrium adsorption isotherm data by using eqs 3b and 4,

$$\epsilon_0 = -\frac{d\sigma_e}{d \ln \Gamma} = RT\Gamma_\infty \frac{\Gamma}{(\Gamma_\infty - \Gamma)} - 2a' \left(\frac{\Gamma}{\Gamma_\infty} \right)^2 \quad (4)$$

where a' denotes a constant originally introduced by Frumkin to describe the interactions between the adsorbed surfactants in the adsorption layer.

It turned out that the experimental elastic modulus values were greater by up to 200% than the “classical” equilibrium values. Interestingly, the deviations occurred exactly within the transitional region of the surfactants’ surface equation of state only.¹¹ This was true for different “classical” types of extended chain amphiphiles which have been repeatedly investigated during the development of surface chemistry, such as *n*-decanoic acid^{1,33–48} and hexadecyltrimethylammonium bromide (CTAB)^{19,49–55} and sodium dodecylsulfate (SDS).^{3,7,13,29,46,50,56–69} The deviations could reasonably be attributed to the amphiphiles’ reorientation within the adsorption layer. Furthermore, it was possible to make conclusions about the dynamics of molecular reorientation, which was of the order of 10^{-6} – 10^{-5} s.

Now coming back to the (i-prop)₃PO amphiphile. A good accordance between experimental and calculated surface elasticity values (Figure 5) is found for low and medium concentrations, i.e., at that region of surface pressure where the extended chain surfactants reveal their characteristic effects of reorientation. Therefore, this result gives ample evidence for the absence of effects of reorientation, as is to be expected from the molecule’s parasol type geometry for suppressing reorientation.

At high concentrations, however, the experimental elastic modulus values are found to be low in comparison with the calculated, classical ones. As effects of reorientation are excluded, any explanation of this discrepancy must first of all take into account the time scale for diffusional exchange.

The fact that at the higher concentrations the dilatational elastic modulus is considerably less than the classical value would suggest that the diffusional exchange time, τ_d , has become considerably less. It is possible that at some values of frequency $\omega\tau_d \ll 1$, causing some relaxation in the value of the dilatational elastic modulus to occur. On calculating the diffusional exchange

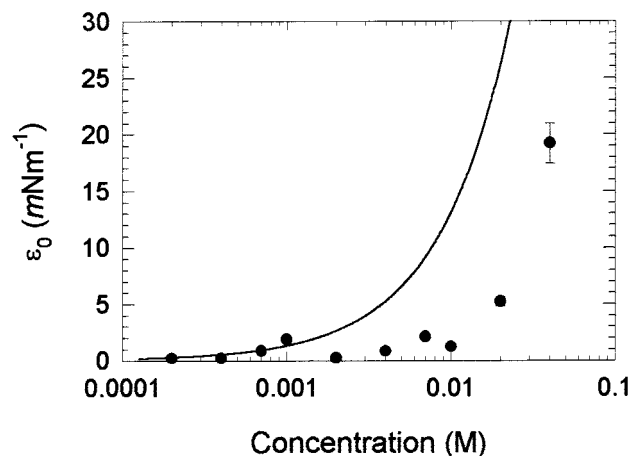


Figure 5. Dilatational elastic modulus values, deduced from the light scattering data, as a function of concentration of aqueous triisopropylphosphine oxide. The line is the variation inferred from the equilibrium isotherm of eq 4.

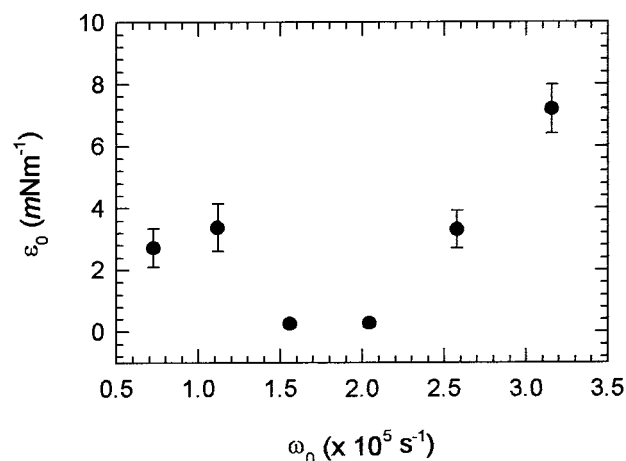


Figure 6. Frequency dependence of the dilatational elastic modulus of a concentration of 2×10^{-3} M aqueous solution of triisopropylphosphine oxide.

time in the concentration region 1×10^{-3} to 4×10^{-2} M, the values were found to vary from 2×10^{-4} to 5×10^{-8} s using eqs 3b and 5,⁷⁰

$$\tau_d \approx 2(d\Gamma/dc)^2/D \quad (5)$$

Therefore, at the higher concentrations, the diffusional exchange is considerably faster than the capillary wave frequencies, so the elastic modulus is partially short circuited by diffusional exchange. For the lower concentrations, the diffusional exchange time and the frequency are of the same order of magnitude, implying some frequency dependence of the elastic modulus. This is indeed occurring at 2×10^{-3} M, as illustrated in Figure 6.

Thus, the fact that the experimental elastic modulus values become lower than the classical ones with increasing concentration can reasonably be explained by some short circuit of the surface tension gradient by diffusional exchange. Table 1 gives the expected values for ϵ_0 from the Lucassen model. These are given at a number of concentrations and expressed as a percentage of the classical values.

However, with respect to this investigation’s goal, the findings at the concentrations where experimental and classical dilatational elastic modulus values in fact coincide are of main importance. The fact that no reorientation effect was observed

TABLE 1: Variation of Dilatational Elastic Modulus Values, Expressed as a Percentage of the Classical Values, with Concentration Due to the Lucassen Model for Diffusional Exchange

concentration (M)	ϵ_0 (% ϵ_{Cl})
2×10^{-3}	80
4×10^{-3}	66
7×10^{-3}	45
1×10^{-2}	31
2×10^{-2}	12
4×10^{-2}	4

in an amphiphilic system, with a particular geometry preventing it from adopting different surface configurations, gives further support to the hypothesis of a transitional region in the equilibrium surface tension vs concentration isotherm of ordinary surfactant systems.

Recently, there is also support from the investigation of electric (surface potential)⁷ and kinetic⁷¹ surface properties for the occurrence of reorientation of surfactants in adsorption layers.

6. Conclusions

Our data illustrates the possibility of blocking the reorientation of surfactant molecules by the design of the molecules. The lack of reorientation is demonstrated by the agreement of the dilatational elastic modulus with the classical value and the absence of a region of considerably higher elasticity values at lower and medium concentrations.

Scheludko's extension⁷² of the relaxation model of Lucassen and van den Tempel⁷⁰ to include molecular reorientation seems to be appropriate in describing ordinary surfactant structures of the *n*-alkyl extended chain type. Thus, surface laser light scattering experiments are very promising for investigating the effects of reorientation in soluble amphiphile's adsorption layers. They not only help to identify the concentration region where it occurs but can also provide interesting new information about the time scale of the accompanying relaxation time. This technique is important since soluble adsorption layers usually miss applications of structure-sensitive methods of investigation, which are commonly used with insoluble spread monolayers.

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