We have investigated alkanethiols, CH₃(CH₂)ₙ-SH (denoted Cₙ) with n = 8, 12, 16, 18, 22 and 30 on clean liquid mercury surfaces by grazing-incidence X-ray diffraction (GIXD), a technique sensitive to the molecular structure within the surface plane, and X-ray reflectivity, which probes the surface-normal electronic density profile. Both techniques have been applied recently to studies of the clean surfaces of liquid mercury³⁰,n and liquid gallium¹⁵, revealing a liquid-like in-plane arrangement of the surface atoms¹⁴, atomic stratification in the surface normal direction and sub-Ångström roughness³¹,₁⁵. R(ω₁), the measured reflectivity profile for wavevector q₁ of the liquid mercury surface covered by Cₙ is shown in Fig. 1 (circles). The data closely follow the reflectivity R₁ of clean liquid mercury at low q₁ and both are only slightly lower than the Fresnel reflectivity R of an ideally flat surface. This indicates a small, surface roughness for the bare and thiol-covered mercury surfaces. At q₁ > 0.5 Å⁻¹, R dips significantly below R₁ but approaches it again at the broad peak around 2.16 Å⁻¹. As this peak characterizes the atomic surface layering of the mercury subphase¹⁴, its persistence for the thiol-covered surface indicates that the organic film induces no major changes in the liquid-metal surface structure. The most significant change, compared with the bare mercury surface, is the emergence of periodic oscillations. The Fresnel-normalized reflectivity (Fig. 2) further highlights these features. The period of the five oscillations observed in Fig. 2a, Δq₁ = 0.25 Å⁻¹, corresponds to a layer thickness d = 2π/Δq₁ = 25 Å, in agreement with the length of a fully extended C₉₉₅₉ molecule. Similar features are observed for thiols of different lengths n. For example, R/R₀ of the C₁₂₁₂ monolayer (Fig. 2b) has a very similar overall shape to Fig. 2a but the oscillation

![Figure 1: X-ray reflectivity from a C₁₂(CH₃(CH₂)₁₀-SH) monolayer-covered (circles) and a bare (dashed line) liquid mercury surface. The Fresnel reflectivity R₁ (solid line) is also shown. The presence of the monolayer is clearly indicated by the oscillatory modulations of the reflectivity. The inset shows the experimental geometry. Alkanethiols were deposited by direct application of the thiols in their liquid state, by chemical vapour deposition, by self-assembly from an ethanol bath, or by spreading from a dilute chloroform solution. All techniques yielded well defined monolayers. X-ray reflectivity measurements at wavelengths 0.5 Å ≤ λ ≤ 1.2 Å were carried out at beamline X22B9 and wiggler beamline X25B at the National Synchrotron Light Source (Brookhaven) at room temperature and under nitrogen. Exposure to the beam was minimized to avoid beam damage. The absolute reflectivity was obtained from measurements along the specular axis (2θ = 0°), subtracted by the diffuse background (measured at 2θ = ±0.6°) and normalized to the direct beam intensity.](image-url)
period is increased to $\Delta q_z = 0.36 \, \text{Å}^{-1}$, corresponding to the shorter length of this molecule $d = 2\pi / \Delta q_z = 17.5 \, \text{Å}$. Oscillations which scale with the length of the C$_n$ molecule have been observed for all thiols studied ($8 \leq n \leq 30$), demonstrating a very similar monolayer structure for all lengths. For long chains ($n = 22, 30$), however, the oscillations are weak and the reflectivity data indicates a high interfacial roughness.

Quantitative information on the atomic arrangement along the surface-normal direction is obtained by fitting the reflectivity data to a density-dependent model reflectivity calculated from the Born approximation. The fitted profiles, displayed as solid lines in Fig. 2 with identical parameters for all data sets (apart from the number of CH$_2$ groups), are in excellent agreement with the experimental data. The corresponding density profiles are shown in Fig. 3. Comparison with the density profile for the clean mercury surface reveals the extended hydrocarbon tail, and the higher-density sulphur atom between the mercury and the hydrocarbon tail. The slight decrease observed in the amplitudes of the first mercury layers probably reflects the small increase in surface roughness expected by the capillary-wave model from a decrease in the surface tension due to the monolayer's presence. Despite this, the general features of a layered mercury surface with an adsorbed, densely packed monolayer of fully extended molecules are found in all the systems studied. Also, the surface roughness (estimated from the density profile width of the first mercury layer) remains about 1 Å, that is, in good agreement with the value given by capillary-wave theory.

Because of the high adlayer density (0.34 ± 0.02 e Å$^{-2}$), which is close to that found in crystalline alkanes and significantly higher than in the melt, in-plane ordering of the molecules might be expected. Despite an exhaustive search at two of the most intense beamlines worldwide, no sharp in-plane peaks corresponding to an ordered adlayer structure were found for the monolayer phases of thiol molecules of any of the examined lengths. In particular, a careful search was done from 1.5 to 1.7 Å$^{-1}$ where structurally similar SAMs and Langmuir monolayers show the lowest-order in-plane peaks. The GIXD data is shown in Fig. 4 for the clean and C$_{18}$-covered mercury surface. Both show the characteristic broad peaks around the in-plane wavevectors $q_i \approx 2.3 \, \text{Å}^{-1}$ and $q_i \approx 4.5 \, \text{Å}^{-1}$ expected for liquid mercury, although at different relative intensities, which may indicate a thiol-induced modification of the mercury surface structure. As we discuss below, the absence of in-plane order in the densely packed alkanethiol monolayer is probably promoted by the disordered mercury subphase via the strong, covalent Hg–S bond. We note that at thiol coverages greater than a monolayer, sharp, resolution-limited in-plane peaks are readily observed, corresponding to the formation of well-ordered multilayer phases (O.M.M. et al., manuscript in preparation).

The results presented here highlight the importance of the relative strengths of the substrate–end-group and inter-chain interactions and the specific order preferred by each. In systems where the latter dominate, such as densely packed films of alkanes, alcohols and fatty acids on pure water$^{1,2,7}$, long-range,
FIG. 4 Grazing-incidence diffraction patterns of a bare (dashed line) and a C$_{60}$ monolayer-covered (bold solid line) mercury surface, measured with an incidence angle $\alpha = 0.2^\circ = 0.6\lambda$ (where $\lambda$ is the critical angle) and a vertical detector acceptance of $0 \leq q_z \leq 1.1\AA^{-1}$ (intensity given in arbitrary units). Here $q_z = 4\pi\lambda \sin \theta/\lambda$ is the in-plane momentum transfer and $\theta$ is defined in Fig. 1 inset. Only the broad peaks corresponding to the mercury liquid structure factor are found in the monolayer data (in-plane resolution $\Delta(2\theta) = 5$ mrad). This data was obtained at the TROIKA undulator beamline of the ESRF\(^{19}\), GIXD measurements at X22B and X25 at NSLS gave similar results.

in-plane order is usually found. This order results not only from the confinement of the monolayer to the water surface, because such in-plane order also appears in alkanes where crystalline monolayers form at the surface of their own melts at temperatures up to a few degrees above the bulk freezing point\(^{19}\). In this case the ‘monolayer’ and ‘subphase’ molecules are identical, and, of course, fully miscible. Both systems are dominated by the inter-chain interactions and the bonds to the sub-phase (~10 kJ mol$^{-1}$ hydrogen bonds in Langmuir monolayers and ~1 kJ mol$^{-1}$ van der Waals interactions in alkanes) are relatively weak. Thus, we conclude that the inter-chain interactions are responsible for the long-range order in these systems. The interactions with the disordered atoms of the liquid subphase tend, in principle, to disrupt this ordering but are too weak to cause more than slight changes in the structure and the phase diagrams of these films.

For SAMs, spatial variations of the interactions with the substrate (corrugation potential) may either promote or oppose the ordering favoured by the inter-chain interactions, depending on the spatial periodicities of both interactions. For alkanethiols on Au(111) (refs 5–7) this corrugation potential favours well ordered monolayers which may be either commensurate or uniaxial incommensurate with the underlying metal. The small mismatch between the underlying substrate and alkane spacings is compensated by a molecular tilt. The elevated melting temperature of C$_{60}$ on Au(111) relative to that of the bulk\(^{19}\) manifests the strong ordering tendency imposed by the interactions with the substrate.

Thiols on mercury ‘feel’ a similarly strong subphase interaction (~200 kJ mol$^{-1}$), but as the liquid mercury surface has no intrinsic long-range order, there is no underlying corrugation potential to order the thiol monolayer. This should promote formation of the order favoured by the inter-chain interaction. If, on the other hand, the ordered thiol layer were to impose its order on the underlying mercury through the strong subphase interaction, with the same structure as found for alkanethiols formed on gold and silver, then the resultant 5–10% compression of the mercury atoms would carry a great energy cost. In addition, this ordered mercury layer, at a temperature where the bulk is disordered, would represent a large increase in the entropic contribution to the free energy of the mercury and for these two reasons seems unlikely. Instead the (liquid-like) subphase surface structure is imposed on the adsorbate film, resulting in an in-plane-disordered film.

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**Prediction of global rainfall probabilities using phases of the Southern Oscillation Index**

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**THE EL NIÑO/SOUTHERN Oscillation (ENSO)** is a quasi-periodic interannual variation in global atmospheric and oceanic circulation patterns, known to be correlated with variations in the global pattern of rainfall\(^{11}\). Good predictive models for ENSO, if they existed, would allow accurate prediction of global rainfall variations, thus leading to better management of world agricultural production\(^{10}\), as well as improving profits and reducing risks for farmers\(^{11}\). But our current ability to predict ENSO variation is limited. Here we describe a probabilistic rainfall ‘forecasting’ system that does not require ENSO predictive ability, but is instead based on the identification of lag-relationships between values of the Southern Oscillation Index, which provides a quantitative measure of the phase of the ENSO cycle, and future rainfall. The system provides rainfall probability distributions three to six months in advance for regions worldwide, and is simple enough to be incorporated into management systems now.

Climate forecast systems offer a means to reduce risks in potentially ‘bad’ years and maximize profits in potentially ‘good’ years. The Southern Oscillation Index (SOI) provides a measure that can be used in developing a seasonal forecast system. The SOI is here defined as the difference in atmospheric pressure anomalies between Tahiti and Darwin divided by the standard deviation of the difference (and multiplied by 10$^{10}$). The SOI is moderately correlated with future seasonal rainfall in some regions\(^{10}\), partly due to the strong auto-correlation between SOI values in early austral winter with those three to six months ahead\(^{11}\). This ‘phase-locking’ of the SOI into the annual cycle permits seasonal forecasting to be attempted once the early stages of various manifestations of the ENSO cycle are underway. In other words,