Study of Molecular Monolayers by Optical Techniques

1. Ellipsometry
2. Infrared Absorption Spectroscopy

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**Monolayer film**: 2-D Physics

1. Melting: Can be a *second-order* phase transition. Theory is easier (dislocation = point defect).

2. Critical point: Different *universality class* from 3-D. Solved models exist (e.g., Onsager, 1944).

3. Computer simulations: More realistic cell size is feasible.

4. Interaction with the substrate lateral periodic structure: Commensurate-incommensurate transitions; New site symmetry.

5. Molecular orientational ordering

6. Mixing (or not) in binary systems
Ellipsometry

\[ \frac{r_p}{r_s} = p \ e^{i\Delta} \]

\[ \Delta \sim \frac{4\pi nd n \cos \theta}{\lambda} \sim \frac{4\pi d}{\lambda} \sim 0.01 \text{ radian (monolayer)} \]
Layer condensation chemical potentials

Chemical potentials relative to bulk solid-vapor coexistence

$$\mu_n - \mu_o = T \ln \left( \frac{P_n}{P_o} \right)$$

$P_n$: pressure at the n-th layer condensation step
$P_o$: saturated vapor pressure
$T_c = 156.2$ K
Frequency shift:

The surface absorption band is shifted from the corresponding band of the free molecule is due interaction with the substrate (chemical shift) and due to interactions between adsorbed molecules, primarily dynamic dipole interaction:

Self-consistent treatment: Each molecule sees the external IR field, plus the field due to all of the other molecules and their images in the conducting surface plane.

1. An isolated molecule sees its own image dipole. This adds to the incident field. That shifts the resonance to lower frequency.

2. Other dipoles in the same plane and normal to the surface subtract from the incident field. That shifts the resonance to higher frequency.
**Dynamic dipole coupling** is treated by a self-consistent field model.

The polarization on site $i$ is

$$p_i = \alpha(\omega)(E_0 + E_i)$$

where $\alpha(\omega)$ is the molecular polarizability, $E_0$ is the external electric field and $E_i$ is the field at site $i$ due to the polarization of all of the other molecules and their images in the surface,

$$E_i = -\sum_{j(\neq i)} U_j P_j$$

If all sites are equivalent, these combine to give

$$p = \frac{\alpha(\omega)}{1 + U\alpha(\omega)} E_0 = \alpha_0(\omega) E_0,$$

where $U = \sum_{j(\neq i)} U_j$ is the dipole sum and $\alpha_0(\omega)$ is the polarizability per molecule of the monolayer. It follows that

$$\frac{1}{\alpha_0(\omega)} = U + \frac{1}{\alpha(\omega)}.$$

For molecules with $N$ relevant vibrational modes,

$$\alpha(\omega) = \alpha_e + \sum_{n=1}^{N} \frac{\alpha_n \omega_n^2}{\omega_n^2 - \omega^2 - i \gamma_n \omega_n \omega},$$

for one mode:

$$\bar{\omega}_1 = \omega_1 \sqrt{1 + \frac{U\alpha_1}{1 + U\alpha_e}}$$
$T = 140 \text{ K}$

$P(\text{SF}_6) = 0.07 \text{ T}$

$0.21 \text{ T}$

$0.63 \text{ T}$
$T = 165\, K$

$P(\text{SF}_2) = 14.0\, T$