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Diffusion and melting of adsorbed monolayers by Mössbauer spectroscopy (*)

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Résumé. — La spectroscopie Mössbauer est appliquée à l'étude des propriétés dynamiques de monocouches adsorbées, avec une attention particulière dans les changements de section efficace d'absorption résonnante produits par la diffusion superficielle. Les systèmes étudiés sont des films de butadiène-Fe-tricarbonyle déposés sur graphite exfolié (Papyex), à plusieurs degrés de recouvrement depuis 130 K jusqu'à la température ambiante. Les spectres d'absorption du Fe57 ont été mesurés dans les directions parallèle et perpendiculaire à la direction moyenne du plan du film. Dans la direction parallèle, l'absorption suit une loi normale en fonction de la température, puis décroit brutalement aux environs de 150 K, indiquant une transition du premier ordre vers une phase fluide. Les résultats sont analysés suivant la théorie du « diffusion broadening » appliquée aux phases bidimensionnelles adsorbées. Les effets de l'orientation des cristallites sont étudiés avec une application spécifique à la texture du Papyex et du Grafoil.

Abstract. — Mössbauer spectroscopy is applied to the study of dynamical properties of adsorbed monolayers with special attention to changes in resonant absorption cross section caused by diffusion along the surface. Specific systems studied were films of butadiene iron tricarbonyl on exfoliated graphite (Papyex) at several coverages, from 130 K to room temperature. The absorption spectra of the Fe57 constituent were measured in the direction parallel to the average film plane and normal to it. In the parallel direction, the temperature dependence of absorption is normal at low temperature, but decreases abruptly to undetectable levels near 150 K, indicating first order phase changes to a fluid phase. The results are analysed in terms of a detailed theory of diffusive broadening in surface films. Effects of crystallite orientation are treated, with specific reference to the partial alignment in Papyex and Grafoil.

1. Introduction. — The physics of adsorbed films has been developing rapidly within the past few years, due principally to the availability of convenient high area uniform substrates together with a more extensive repertory of experimental techniques [1, 2]. Neutron and electron diffraction, coupled with calorimetry and vapour pressure measurements have, in several systems of van der Waals films adsorbed on basal plane graphite, yielded highly detailed descriptions of distinct monolayer phases and their transformations. These studies have presented microscopic views of the local structural arrangements of the adsorbed atoms and their positions relative to the substrate. Dynamical properties of monolayers have not been as deeply explored as yet, although a number of important studies should be noted. Debye Waller factors along directions parallel and perpendicular to the film plane have been measured by low energy electrons [3], neutrons [4], and Mössbauer resonance [5, 6]. Inelastic neutron scattering has been employed to determine spectra of collective modes [4, 7, 8] and of the internal vibrations of adsorbed organic molecules [9]. Diffusion coefficients have been measured by line broadening of quasi elastic neutron scattering [10]. Changes in mobility and diffusion
The Debye Waller factors of monolayers may have unusual temperature and coverage dependence, relating to their correspondence with two-dimensional solids. The nature of melting in films involves several questions which remain unresolved at this time; whether changes in mobility are coupled with structural transitions as in bulk matter, to what extent the order of the phase change is dependent on registry with the substrate, and the relevance of various two-dimensional models. Such questions, at least in part, can be addressed by techniques of Mössbauer spectroscopy. Mössbauer spectroscopy is well known for its application in bulk systems, as for example the exploration of vibrational spectra through measurements of Debye Waller factors and thermal shifts [13, 14]. Such measurements have been made on a few monolayer systems, and have yielded detailed information about the atom-substrate forces and the nature of the adsorbed phases [5, 6]. Mössbauer spectroscopy has also been used to investigate diffusion in bulk glasses and supercooled liquids [15, 16]. It is not suitable for typical liquids, where the diffusion rates are too high for detectable resonance cross sections. In monolayers, however, the effective line broadening due to diffusion can be less. Diffusion constants in the plane of the film may be considerably smaller than in the bulk phase. Moreover, for aligned substrates such as Grafoil, the diffusion in the film plane can be detected but effectively attenuated by geometrical factors when observed along other directions. This permits the use of Mössbauer spectroscopy to probe into the mobile states of films, and to observe changes in mobility in the neighbourhood of melting transitions. A brief report on such a study has been published [17]. This paper describes the work in more detail, together with unpublished results and a theory of the experiment.

2. Experimental details. — The systems studied were monolayers of 1,3-butadiene iron tricarbonyl (BIT) adsorbed on Papyex. This combination of adsorbate and substrate was chosen as particularly convenient for studies of solid and liquid monolayers by Mössbauer spectroscopy.

BIT is one of a class of carbonyl organometallic compounds which are relatively stable at room temperature and below, with weak intermolecular forces and low boiling and freezing points. This particular compound, C₄H₆Fe(CO)₃, boils at 48 °C and freezes at 19 °C [18]. Its vapour pressure at room temperature is about 1 torr, hence it can be controlled and deposited on cold substrates by essentially the same techniques used for the more commonly studied absorbates that are gaseous at room temperature. The iron atom in each molecule is an internal constituent. The molecular structure, determined by ultraviolet and infrared spectroscopy [19, 20], is shown in figure 1. In this structure, the butadiene hydrocarbons define a plane. The iron lies outside this plane and is roughly equidistant from the four carbons of the butadiene. The iron probably forms a tetrahedron with the three carbonyl groups.

Fig. 1. — Molecular structure of 1,3-butadiene iron tricarbonyl, C₄H₆Fe(CO)₃. The butadiene hydrocarbons form a plane, but the spacings between the 4 carbons are not all equal. The iron atom lies outside the butadiene plane, roughly equidistant from the 4 carbons. The 3 CO groups are believed to form a tetrahedron with the iron [19, 20]. In this perspective view the molecule is shown with the butadiene ring resting on a basal plane net of graphite.

Iron is an especially convenient atom for Mössbauer studies. Its isotope Fe⁵⁷, which has normal abundance ~ 2%, has a combination of nuclear properties which has made the material one of the most useful in studies of bulk properties. Mössbauer studies have been made on bulk BIT at 78 K and at 4.2 K, reporting the shift and quadrupole splitting of relatively weak resonance lines [21, 22].

Papyex is a high area graphite adsorbent similar to Grafoil [1, 23]. It consists of crystallites of exfoliated graphite having primarily basal plane facets exposed for adsorption, rolled into binderless flexible sheets, with density about 1 g/cm³ and adsorption area 20 m²/g. The crystallites are oriented preferentially with basal planes parallel to the rolling direction; the angular distribution of adsorption area determined by neutron diffraction has a width of 30° FWHM about the average normal to the sheet for 50% of the area, and random orientation of the remainder [24, 25]. Chemical stability, adsorption uniformity and reproducibility of Grafoil and Papyex are excellent, as indicated in numerous studies [1].
The Papyex substrate in the present Mössbauer study consisted of a 16 gram stack of sheets in a special transmission cell described below. The stack was first cleaned by heating in vacuum at 975 °C, and then loaded into a system for measuring adsorption vapour pressure isotherms. Isotherms of N₂ at 78 K and of BIT at room temperature gauged the adsorption area and provided comparisons with other more detailed BIT isotherms that were measured on another sample. The N₂ isotherm indicated an effective area of about 340 m² for the 16 gram stack, i.e. 21.2 m²/g. The BIT isotherms, illustrated in figure 2, indicated monolayer completion at about 40 (Å)² per molecule. This value agrees closely with the effective area 42 (Å)² corresponding to the bulk liquid density at 20 °C and with the results of strain gauge spreading pressure measurements (see Sect. 3. 2), which indicate completion at 41.5 (Å)² at room temperature.

After the BIT isotherms, the Papyex stack was cleaned again and then transferred under inert gas to the transmission cell. It was checked by Mössbauer transmission to verify that no BIT or iron remained after cleaning. The cell was then charged with 0.3 monolayer of BIT and installed in the cryostat. Spectra were studied at selected temperatures, with gamma ray transmission vector parallel and perpendicular to the plane of the sheets. The sequence was repeated for each coverage.

Figure 3 shows details of the cell. The Papyex sheets are loaded with planes vertical in compartment C; this chamber is of copper measuring 25 x 25 x 37 mm internal dimensions. Two sets of Mylar windows permit transmission with gamma ray vector k, parallel or perpendicular to the plane of the sheets. The cell is charged with adsorbate gas through the valve a. Temperature is controlled and measured by means of heater d, thermometer i, and cooling link f, h to the refrigerant bath g.

The gamma ray source was a thin foil of rhodium containing a dilute solid solution of Co⁵⁷ with initial activity 25 mCi. The source line width was only 10 % greater than natural width, 0.099 mm/s, and had a resonant fraction at room temperature of 0.76 of the 14 keV radiation. The effective thickness of the Papyex in the transmission cell, for both the 14 keV and non-resonant 6 keV radiation, was found to be the same in both directions, to within 6 %. A conventional spectrometer was used for all measurements.

3. Experimental results. — 3. 1 Mössbauer spectra. — We obtained Mössbauer spectra at closely spaced temperatures for each film coverage, X = 0.3, 0.6 and 1.0 monolayers, and for a sample of bulk BIT. Figures 4, 5, 6 show examples of the spectra of the films, at selected temperatures. In each graph « 1 » and « / » refer to the directions of the gamma ray

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Fig. 2. — Vapour pressure isotherms of butadiene iron tricarbonyl (BIT) on Papyex graphite. Monolayer completion, as judged from the conventional point B method, is estimated to occur at about 40 (Å)² molecular area. More precise estimate of completion points were obtained by strain gauge measurements (see Fig. 11).

Fig. 3. — Schematic drawing of the gamma ray transmission cell. Copper chamber C contains the stack of Papyex sheets oriented with planes vertical. Two sets of mylar-covered windows allow transmission of γ-rays parallel or perpendicular to the Papyex planes. The cell is charged through the valve a. Temperature is controlled and measured by means of heater d, thermometer i, and cooling link f, h to the refrigerant bath g.
Fig. 4.—Mössbauer transmission spectra of adsorbed BIT at coverage $X = 0.3$. Symbols « $\parallel$ » and « $\perp$ » refer to $\gamma$-ray transmission direction relative to the Papyex planes.

Fig. 5.—Mössbauer transmission spectra at coverage $X = 0.6$. The two directions, which could be obtained by a simple 90° rotation of the cryostat about its vertical axis, were usually studied in quick succession so as to keep the experimental conditions nearly the same. The spectra for each coverage, temperature and direction were usually collected in 20-30 minutes, which yielded $10^6$ counts per velocity channel. This yielded a reasonable statistical spread in view of the low absorption. The data were computer least squares fitted to two Lorentzian lines, with no restrictions placed on the line width, location or intensity. Measurements of the line widths, splittings and absorption intensity were made from the computer fits.

Comparisons between the spectra in figures 4, 5, 6 show several interesting features. The line shapes and splittings for the two directions are similar, particularly at low temperature. Not shown are the spectra for solid BIT, but we note here that the patterns resemble the bulk spectra taken in our study, and have similar parameters to those previously published [21, 22]. The two computer fitted lines have appreciably different widths, the line at positive velocity being consistently broader in all samples including the bulk. The intensities in the fitted lines are unequal but the difference is not large or consistent in direction. At low temperature, the intensities in the two directions are comparable, but they become markedly different as the temperature is raised. Absorption decreases more rapidly in the parallel direction, becoming practically zero between 150 K and 160 K. In the perpendicular direction, there is noticeable absorption at least up to 200 K. By comparison, the absorption in the bulk solid seemed less strong; even in our relatively thick sample, there was no perceptible absorption at 230 K.

Our principal quantitative results involve the intensities of the absorption spectra, i.e. the integrated
areas of the resonance dips. For thin samples, these areas are proportional to the resonant cross section, and this condition holds for all of the film samples. Applying standard techniques for the subtraction of non resonant background intensity, we obtained the results shown in figures 7 and 8. The two sets are dramatically different: while the temperature dependences have essentially normal appearances in the perpendicular direction (compare with the bulk solid results, figure 7), the parallel direction shows sudden drops to zero absorption in each film, near 150 K. On closer inspection, one can see small decreases of absorption in the perpendicular direction, coincident with the catastrophic drops of the parallel signals. The detailed explanation of these changes is given in the next section and in sections 4 and 5. At this point, we merely note that the sudden drops are interpreted as due to melting transitions, which cause large increases in surface diffusion rates. The diffusion is primarily effective in the lateral direction, but a small effect is also seen in the normal direction, due to crystallite misorientations and the finite angular geometry of the experiment.

3.2 VAPOUR PRESSURE AND SPREADING PRESSURE. — The isosteric heat of adsorption (conventionally $q_a$) is one of the primary thermodynamic parameters in an adsorption system. It can be obtained from a series of vapour pressure isotherms taken at closely spaced temperatures, via the general relation [1]

$$q_a = - k_B \left[ \frac{\partial \ln P}{\partial (1/T)} \right]_a$$

(1)

where $a$ is the average area per molecule. In the present study, we obtained isotherms at only 3 temperatures and hence it was necessary to verify that the logarithmic derivative was approximately constant in order to deduce $q_a$ from the differences. As may be seen in figure 9, the slopes appear satisfactory. The slopes fall into 2 distinct groups; those for coverages below a completed monolayer and those above. The corresponding heats of adsorption are listed in table I. In typical systems of physisorption, $q_a$ for $X < 1$ is greater than for higher coverages, except for a relatively narrow peak just around $X = 1$. By
Table I. — Adsorption energy $e_0$ and heat of adsorption $q_{st}$ of butadiene iron carbonyl on Papyex graphite. Energies $e_0$ were determined from $\gamma$-ray absorption at low temperature, while $q_{st}$ was measured from vapour pressure isosteres at room temperature.

<table>
<thead>
<tr>
<th>Coverage (X)</th>
<th>$e_0$ (s$^{-1}$)</th>
<th>$e_0$ (kcal/mole)</th>
<th>$q_{st}$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>4.9 $\times$ 10$^{12}$</td>
<td>12</td>
<td>5.3</td>
</tr>
<tr>
<td>0.63</td>
<td>5.6 $\times$ 10$^{12}$</td>
<td>15</td>
<td>5.5</td>
</tr>
<tr>
<td>1.04</td>
<td>7.7 $\times$ 10$^{12}$</td>
<td>28</td>
<td>16.0</td>
</tr>
<tr>
<td>1.30</td>
<td></td>
<td></td>
<td>12.9</td>
</tr>
</tbody>
</table>

contrast, in the present system $q_{st}$ is distinctly greater at $X = 1$ and $X = 1.3$ than at submonolayer coverage, indicating that the 2-layer films are more stable. As will be seen below, the binding energies deduced from the gamma ray resonance intensities indicate the same trend.

Determination of adsorption binding energies by Mössbauer resonance has been described previously [5, 6]. Details will not be repeated here, but the basis can be briefly described. The general scheme is based on measurement of resonant absorption cross section of a film for gamma rays directed normal to the surface. Since absorption cross section in general proportional to mean squared displacement of the resonant atom in the $k_y$ direction, this measurement depends on motion of the adsorbed molecule in the direction perpendicular to the substrate. For small vibrations about the minimum, the potential can be expanded in a power series and truncated after the quadratic term. In this approximation, one can obtain a simple expression for the binding energy in terms of the frequency and equilibrium position of the atom. For a 6-12 Lennard-Jones potential, a molecule of mass $m$, equilibrium distance $Z_0$ and frequency $\omega$ has binding energy $e_0$

$$e_0 = m\omega^2 Z_0/27.$$  

The Debye Waller factor for the same simple model is readily obtained:

$$\ln f = -4\pi^2 k_B T/m\omega^2 \lambda.$$  

Thus measurement of the resonant fraction $f$ in the normal direction, together with estimate of $Z_0$, can yield $e_0$.

In molecules with appreciable internal motion, the resonant fraction is further reduced. To avoid the effects of intramolecular displacements, at least to first order, one takes the first temperature derivative of the resonant intensity. If the intramolecular motion is incoherent relative to the molecule-surface vibration, the resonant fraction is a simple product

$$f = f_{int} f_{ext},$$

in which case eq. (3) represents only $f_{ext}$. Since typical internal motions have relatively high frequencies, their temperature dependences are correspondingly weaker; consequently the temperature dependence of the total resonant fraction is dominated by the part due to $f_{ext}$. An additional advantage to the temperature derivative is that it avoids effects due to errors in background corrections and other constant factors. Accordingly, our values for $e_0$ determined by this method are listed in table I. For the distance $Z_0$, we estimated

$$Z_0 = R + C/2$$

where $R$ is the mean radius corresponding to the liquid density at 20 °C, and $C$ is the C-axis spacing of graphite. It can be noticed that $e_0$ is distinctly larger for $X = 1$ than for lower coverages, consistent with the trend of $q_{st}$. The two sets of values are comparable but not equal, nor is it expected that they should coincide. It is only for isolated atoms at 0 K that $q_{st}$ and $e_0$ are the same; then both are equal to the single atom-substrate binding energy. In general, $e_0$ also contains the binding energy to the other atoms of the film, and $q_{st}$ contains contributions due to entropy difference between the adsorbed and gaseous phases.

We used a surface strain gauge to measure the two-dimensional spreading pressure of BIT films at room temperature, in order to check the estimates of monolayer density and to determine some of the characteristics of the first two layers. The instrument [26] indicates the dilatation of a Grafoil or Papyex substrate caused by adsorption. In simple cases of non registered films, the dilatation is proportional to the conventional thermodynamic or Gibbs spreading pressure, but it is in general more complicated when changes in the substrate structure are involved. We believe that the large size of the BIT molecule, together with the relatively weak binding energy, leads in this case to the more simple situation. The results of the strain gauge measurements are shown in figure 10. The curve

![Figure 10](image-url)

Fig. 10. — Spreading pressures $\varphi$ of BIT on Papyex at 20 °C, determined from strain gauge measurements. The form of the curve at coverages smaller than $X = 1$ suggests an imperfect 2D gas. At higher coverage, the decreased slope indicates an enhanced attraction.
is quite similar to those observed previously with light organic molecules at room temperature [26]. Its form suggests an imperfect two-dimensional gas above its critical temperature, and therefore as in the original work we analysed the results by a truncated virial series:

\[
\frac{\varphi a}{kT} = 1 + \frac{B}{a} + \frac{C}{a^2}
\]  

where \( \varphi \) is the measured spreading pressure. \( B \) and \( C \) are the second and third virial coefficients, respectively. If eq. (5) is obeyed a plot of \( (\varphi a/kT - 1)/a \) versus \( 1/a \) should be a straight line. Figure 11 shows that it is at low coverages, with a section of another straight line above \( X = 1 \). The intersection is at \( a = 41.5 \) (Å)², i.e. at a value consistent with first layer completion as deduced from the vapour pressure isotherms. Similar breaks in slope were seen at monolayer completion (deduced from molecular sizes) in the earlier strain gauge study. The two distinct regions indicate that the second layer acts as a substance different from the first. Both appear on this view to be effectively two-dimensional gases, but with different virial coefficients: from the slopes and intercepts we obtain

\[
\begin{align*}
B_1 &= -3.1 \times 10^2 \text{ (Å)}^2, & C_1 &= 1.8 \times 10^4 \text{ (Å)}^4, \\
B_2 &= 2.1 \times 10^2 \text{ (Å)}^2, & C_2 &= -3.9 \times 10^3 \text{ (Å)}^4.
\end{align*}
\]

4. Theory of resonant absorption by surface films. — The general theory of resonant emission and absorption spectra has been given by Singwi and Sjölander [27]. They applied the theory to several specific models of three dimensional solids and liquids, with particular emphasis on the effects of atomic diffusion. Here we adapt their theory to corresponding models of films; first to planar films and then to films on partially oriented substrates and these models to interpret the experimental results.

The effect of diffusion on resonance is primarily a broadening of the emission or absorption line. The line shape and its angular dependence in anisotropic media depend on the nature of the atomic diffusion. Two types of diffusion are treated here: liquid-like diffusion as in a classical fluid, and jump diffusion of a crystalline solid. In part (iii) we treat harmonic solid models.

(i) Two dimensional classical liquid. — The general expression for a classical fluid resonant cross section \( \sigma_{\text{res}} \) at resonance is, after eq. (37) of reference [27],

\[
\sigma_{\text{res}} = \frac{\bar{K}(T)}{2 \pi r \sqrt{\pi D t}} \exp\left[ -\frac{r^2}{4 D t} \right]
\]

where \( \bar{K} \) is the wave number and \( \Gamma \) is the energy width of the gamma ray. \( F_0(t) \) is the classical self-diffusion function, i.e. the probability that a particle initially at \( r = 0 \) diffuses to \( r \) in time \( t \). The coefficient \( \bar{K} \) is a function of the temperature and single particle quantities; at resonance it is

\[
\frac{\bar{K}(T)}{4 \hbar} = \frac{\sigma_0 \Gamma}{4 \hbar} \exp\left[ -\frac{\hbar^2 k^2}{8 m k_B T} \right].
\]

For a two dimensional classical liquid, a solution of the diffusion equation for large \( r \) is [28]

\[
F_0(t) = \frac{1}{2 \pi r \sqrt{\pi D t}} \exp\left( -\frac{r^2}{4 D t} \right)
\]

where \( r \) is the displacement vector in the plane of the surface. Substituting (8) in (6), we have

\[
\sigma_{\text{res}} = \frac{\bar{K}}{2 \pi \sqrt{\pi D}} \int l^{-1/2} \times
\]

\[
\exp\left[ ik' r \cos \varphi - \frac{\Gamma |t|}{2 \hbar} - \frac{r^2}{4 D t} \right] dr \, dt \, d\varphi
\]

where \( k' = k \sin \theta \) is the component of \( k \) in the plane of the film. The integration over \( r \) can be carried out by transforming the exponential to a Gaussian, with limits \( 0 \leq r \leq \infty \), which yields

\[
\sigma_{\text{res}} = \frac{\bar{K}}{2 \pi} \int \exp\left[ -D k'^2 \cos^2 \varphi t - \frac{\Gamma |t|}{2 \hbar} \right] dt \, d\varphi.
\]

Successive integrations with limits

\[
0 \leq t < \infty, \quad 0 \leq \varphi < 2 \pi
\]

yield

\[
\sigma_{\text{res}} = \frac{2 \hbar \bar{K}}{\Gamma} \left( 1 + \eta \sin^2 \theta \right)^{-1/2}
\]

where \( \eta = 2 \hbar D k^2 / \Gamma \).
The significance of $\eta$ can be given in simple terms. Since the diffusion coefficient $D$ is the mean squared displacement per unit time, during the lifetime $\tau(=2h\Gamma)$ of the $\gamma$-ray, a particle diffuses a mean distance $R_\tau \sim \sqrt{D\tau}$. Therefore the parameter $\eta$ involves the ratio between this distance and the wavelength $\lambda$ of the radiation:

$$\eta \sim \left(2\pi R_\tau/\lambda\right)^2.$$  

(12)

The importance of diffusion in isotropic three dimensional media involves $D$, $\tau$ and $\lambda$ in the same way: if $\eta \ll 1$ diffusion has little effect on line width and cross section, while fast diffusion corresponds to $\eta \gg 1$. For surface films, there is an angular dependence as well; eq. (11) shows that if $\eta \gg 1$, the effects of diffusion can be changed from the fast diffusion regime to the slow diffusion limit as $\theta$ is varied from $\pi/2$ to 0. For the relevant motion is just the component of displacement along the $k$ direction, and it is therefore possible in principle to eliminate diffusion broadening by measuring in the surface normal direction. Such control is limited in practice, however, by both the finite angular resolution of reasonable experimental arrangements, and by the distribution of surface orientation in adsorbents, which is usually more serious. For the general case of interest, we will assume that a film is composed of regions which are planar on a scale which is large compared to the diffusion length $R_\tau$. The resonant absorption in each planar region therefore obeys eq. (11), according to the individual orientations $\theta$ with respect to the common $k$ direction. If the normalized distribution function of orientations of adsorption area is $f(\theta)$, then the average cross section $\overline{\sigma}$ for an entire sample is

$$\overline{\sigma} = \int_0^{\pi/2} f(\theta) \sigma(\theta) \sin \theta \, d\theta.$$  

(13)

We next examine a few specific distribution functions representing practical adsorbents.

a) Random orientation. — With random orientations $f(\theta) = 1$, and we obtain directly from (11) and (13):

$$\overline{\sigma}(\eta \ll 1) = \frac{2h\sqrt{\eta}}{\Gamma \sqrt{\eta}} \sin^{-1} \left(\frac{\eta}{\sqrt{1 + \eta}}\right).$$  

(14)

For slow diffusion $\eta \ll 1$, the function $\sin^{-1}$ can be approximated by its argument, and we obtain

$$\overline{\sigma}(\eta \ll 1) = \sigma_0 = \frac{2h\sqrt{\eta}}{\Gamma}.$$  

(15)

In the fast diffusion regime, the arcsine tends to $\pi/2$, which yields

$$\overline{\sigma}(\eta \gg 1) = \frac{\pi h\sqrt{\eta}}{\Gamma} = \frac{\sigma_0}{\sqrt{\eta}}.$$  

(16)

Thus for fast diffusion, the average cross section is markedly reduced, varying as $D^{-1/2}$.

b) Aligned adsorbents. — In certain practical adsorbents, there is a preferential orientation about some common direction, e.g. the direction normal to the plane of the sheet in Grafoil and Papex. To model these cases most simply, we use a square distribution, i.e. a distribution of angles equal to a constant within a range $\theta_0 \pm \Delta \theta$, and zero outside of the range. The average cross section is found to be

$$\overline{\sigma}(\eta \ll 1) = \frac{\sigma_0 \sin \Delta \theta}{\Delta \theta}.$$  

(18)

For fast diffusion, we obtain

$$\overline{\sigma}(\eta \gg 1) = \frac{\sigma_0}{\sqrt{\eta} \sin \theta_0}.$$  

(19)

The divergence of (19) at $\theta_0 = 0$ presents no practical difficulty since in actual measurements there is a finite angular resolution. If the collimation divergence is some small angle $\Delta \theta$, then the minimum value of $\sin \theta_0 \approx \Delta \theta$ and the average cross section in the $\theta_0 = 0$ direction is

$$\overline{\sigma}(\eta \gg 1)_{\theta_0 = 0} \approx \frac{\sigma_0}{\sqrt{\eta} \Delta \theta}.$$  

(20)

The empirical distributions in Grafoil and Papex consist of a mixture of random orientations and a narrow peak [24, 25]. The average cross section for such samples is simply a superposition of the results in sections (a) and (b) above.

(ii) Stepwise diffusion. — The diffusion of atoms in a crystalline solid is characteristically a hopping motion; an atom resides for some time at a well-defined site before jumping to a new site at a discrete distance away. Singwi and Sjölander show that if there is no correlation between the motion of one jump and the next, the resonant absorption cross section is

$$\sigma_{res} = h\sqrt{kG} | \Gamma + \Delta \varepsilon |^{-1}$$  

(21)

where $\sqrt{kG}$ is the same coefficient as given by (7). The quantity $\Delta \varepsilon$ is the complex line width caused by the diffusion:

$$\Delta \varepsilon = \frac{2h}{\tau_0} \left[1 - \int e^{ikr} g(r) \, dr\right]$$  

(22)
where $\tau_0$ is the mean residence time on a site and $g(r)$ is the probability for an atom initially at the origin to move to $r$ in one jump.

We can apply the theory to a simple but general model of stepwise diffusion in a film. Assume that the probability is isotropic in the surface plane and that all jumps are of equal length. The length in such a model is plausibly equal to $r_0$, the nearest neighbour distance, hence $g(r)$ is a $\delta$-function $\delta(r' - r')$ where $r'$ is the two dimensional displacement. With the angle $\theta$ as the inclination between the surface normal and the wavevector $\hat{k}$ as before, we obtain

$$\Delta \varepsilon \approx \frac{2}{\tau_0} \left[ \frac{2 \hbar}{r_0} \right] \sin \left( \frac{kr_0}{2} \sin \theta \right).$$

In the surface normal direction $\theta = 0$ and $\Delta \varepsilon = 0$. The width increases with angle to a maximum in the surface parallel direction as in the case of liquid-like diffusion. The angular dependence is different in this case, however; we can illustrate it best by inspecting the case of fast diffusion, i.e. where the maximum diffusion width is much greater than $\Gamma$. In this case, the total width is approximated by

$$|\Delta \varepsilon| \approx \frac{4 \hbar}{\tau_0} \left| \sin \left( \frac{kr_0}{2} \sin \theta \right) \right|.$$

If the jump distance is relatively small, i.e. $r_0/\lambda \ll 1$, then the angular dependence becomes simply $|\sin \theta|$:

$$|\Delta \varepsilon| \approx \frac{2 \hbar r_0}{\tau_0} |\sin \theta|.$$ (25)

In this case, the cross section has the same angular dependence as for a liquid in the fast diffusion regime. A distinction emerges as the jump distance becomes comparable to a wavelength. Actually, the relevant parameter is $k r_0$, which contains a factor $2 \pi$; in the case of the 14 keV $\gamma$-ray of Fe$^{57}$, $k \sim 7 \text{Å}^{-1}$, so that $k r_0$ in typical solids is greater than 10. For the molecular films of butadiene iron carbonyl, the factor $k r_0/2 \approx 20$. In such circumstance, the line width as a function of $\theta$ has a very narrow central minimum; the angular width of this minimum is approximately equal to $(k r_0)^{-1}$. At larger angles, the width oscillates rapidly between 0 and its maximum value $2 \hbar k r_0/\tau_0$. These oscillations may occur in individual atoms but cannot be seen in a macroscopic sample. The oscillations arise from phase shifts greater than $2 \pi$, bringing the radiation into repeated resonance as the components of displacement along $\hat{k}$ become equal to multiples of a wavelength. In real situations, the absorption is an incoherent superposition by a large number of atoms, and the total effect averages out the high frequency oscillations. The central minimum near $\theta = 0$ remains, however, so that the net result is a cross section with a very narrow peak, decreasing to negligible values beyond. This type of angular dependence is quite unlike the gradual $(\sin \theta)$ variation for liquid-like diffusion, and hence it might provide a definitive test distinguishing stepwise diffusion from the liquid variety.

The sharp angular dependence is of course attenuated in partially aligned adsorbents, but depending on the degree of alignment and the magnitude of the coefficient $k r_0$, a narrow dependence may remain. The details of the averaging for such partially aligned adsorbents follow the same principles as in (i) above.

(iii) Harmonic forces. — Resonant absorption and emission spectra in harmonically bound materials are characterized by a clear distinction between a sharp zero phonon fraction $f$ and a very broad remainder containing all of the processes involving phonon absorption and creation. The sharp fraction depends exponentially on the mean squared amplitude of vibration along the $\hat{k}$ direction

$$\ln f = -\langle (\delta \hat{z})^2 \rangle$$ (26)

where the angular brackets denote thermal average. Eq. (26) is a classical approximation and is obeyed by most systems of interest at temperatures above a few tens of Kelvin [13]. It is readily applied to situations in adsorption, where the mean squared amplitude of vibration is typically quite anisotropic. The application of [26] to motion in the surface normal direction, briefly described in section 3.2, depends on a harmonic approximation to the shape of the holding potential over the region of the amplitude of vibration. As discussed in detail in references [5] and [6], the approximation is satisfied quite well in typical adsorption systems.

We therefore assume a monolayer film with relatively strong harmonic binding to the substrate and different isotropic forces along the surface. If $\theta$ is the angle between $\hat{k}$ and the surface normal, (26) becomes

$$\ln f = k^2 \left[ \langle \delta z^2 \rangle \cos^2 \theta + \frac{2}{\pi} \langle \delta \rho^2 \rangle \sin^2 \theta \right]$$ (27)

where $\delta \rho^2 = \delta x^2 + \delta y^2$ is the mean squared displacement in the surface plane.

If we define $(\ln f)_\rho$, and $(\ln f)_\rho$, to be the sharp resonant fractions measured in the directions parallel to the plane and along the $z$ axis, then for arbitrary $\theta$

$$(\ln f)_\rho = (\ln f)_\rho \sin^2 \theta + (\ln f)_\rho \cos^2 \theta.$$ (28)

In partially aligned adsorbents the angular dependence is an average over the distribution, as in the previous cases. We illustrate the averaging effect by treating a specific distribution which approximates the empirical distribution of Grafoil indicated by neutron diffraction (see Section 1). For a random distribution, the average value of $\ln f$ is, from (28)

$$(\ln f)_{\text{random}} = \frac{2}{3} (\ln f)_\rho + \frac{1}{3} (\ln f)_\rho.$$ (29)
For the sharp fraction with relatively narrow width, the peaked portion can be approximated by a delta function about the inclination \( \theta_0 \) with respect to the surface normal, i.e.

\[
(\ln f)_{\text{sharp}} = (\ln f)_0 \sin^2 \theta_0 + (\ln f)_{\perp} \cos^2 \theta_0.
\]  

(30)

Adding the two portions in equal amounts, one obtains

\[
(\ln f)_0 = \frac{4}{3} (\ln f)_{\parallel} - \frac{1}{3} (\ln f)_{\perp}
\]

\[
(\ln f)_{\perp} = \frac{5}{3} (\ln f)_{\parallel} - \frac{2}{3} (\ln f)_{\perp}.
\]  

(31)

5. Analysis of resonant fraction. — 5.1 Low temperature regime ; two dimensional solids. — The theory of section 4 is now applied to the analysis of the data. In the low temperature range, \( T < 140 \text{ K} \), the smooth monotonic behaviour of the absorption in both directions suggests solid-like behaviour, i.e. that the films, in addition to being strongly bound to the substrate, are also elastic in the plane of the film. In this case, the resonant fraction can be expressed in terms of the mean squared displacement in the plane of the film. Two quite distinct types of solid-like film are foremost among current models. In a registered solid, the atoms are localized within the potential wells provided by the substrate, while in a two dimensional solid, the atoms are localized by their interactions with neighbouring adsorbed atoms. In the former case, the mean squared displacement varies exponentially with \( T \) at low temperature, tending toward linear dependence at high \( T \), similar to the surface-normal motions. But a two dimensional solid has a linear dependence on \( T \) at low temperature, due to the continuum of low lying modes extending to very low frequencies. For infinite two dimensional media, the spectrum extends all the way to \( \omega = 0 \), which causes the mean squared displacement to be divergent. However, in finite systems, there is a low frequency limit given by the size of the system [29].

The simplest model for calculation is a two dimensional Debye solid, for which \( g(\omega) \) is proportional to \( \omega \). Introducing the lower limit, we have

\[
g(\omega) = \frac{4 N_0}{\omega_0^3} \frac{2 \pi}{L} \leq \omega < \omega_0
\]  

(32)

where \( \omega_0 = k_{\text{B}} \theta / h \) is the Debye limit and \( L \) is the linear dimension of the sample. The resonant fraction is found to be:

\[
f_{\text{r}} = \exp \left[ - \frac{(h k_{\text{B}})^2 T \ln N^*}{2 m k_{\text{B}} \theta^2} \right].
\]  

(33)

We find that the data can be well fitted to a function having the temperature dependence of eq. (33), and therefore it cannot be decided, from this fact alone, whether the film is localized or not. However, the size of the molecule relative to the substrate mesh makes registry unlikely, and hence on this basis it is more reasonable to interpret the films in terms of an elastic continuum, i.e. a Debye model. A further consideration is the question of internal motions of the Fe\(^{57}\) atoms in the molecule. These modes, as discussed earlier in connection with the surface-normal vibrations, may reasonably be expected to have relatively high frequencies and hence weaker temperature dependence than the intermolecular modes. Therefore, in order to eliminate the effects of the zero point intramolecular motions, we differentiate the intensity data, and then compare the results with the temperature derivative of eq. (33). In order to apply eq. (33), we must estimate the sample size \( N \). Here we assume that the film is divided into domains having the same characteristic dimension that has been deduced for several types of adsorbates, with several experimental techniques on Grafoil and Papyex substrates, i.e. about 100 A linear dimension [1, 4, 26]. This corresponds, for the full coverage BIT film, to \( N \approx 240 \). Finally, we obtain from the \( X = 1.04 \) data for \( (\ln f)_{\parallel} \) : \( \theta = 59 \text{ K} \). The two monolayer films yield comparable values, but with small differences depending on our interpretation of the actual states of the samples. If the films are assumed, at submonolayer coverage, to be in the form of solid islands, then the corresponding values of \( N \) can either be taken to be the same as the full coverage value (domains are either completely full or empty), or proportionately reduced according to the mean coverage (domains are partially covered with islands of uniform density). If, however, the entire surface is uniformly covered, the corresponding densities of the film are proportional to the average coverage, and the population of each domain is accordingly reduced. Of these choices it seems that only the last is tenable in view of the changes in melting temperature. If the films were in the form of solid islands, they would all melt at a single temperature, i.e. the two dimensional triple point. Therefore, we calculate \( N \) on the basis of proportionality to coverage ; the corresponding values for the submonolayer samples are : \( X = 0.63, \theta = 58 \text{ K} \); \( X = 0.33, \theta = 54 \text{ K} \). It cannot be said whether this slight shift is a real effect, but it should be noted that the variation is in the normal direction for most bulk materials and in the few monolayer systems that have been measured to date [1, 30].

5.2 Surface diffusion ; two dimensional melting. — The most dramatic effects are seen in the region between 140 K and 160 K, where each sample exhibits a sudden loss of resonant absorption in the surface parallel direction. Our interpretation involves an effective melting of the two dimensional solid, entailing an abrupt increase in surface diffusion and consequent line broadening. However, no large changes in width are observed in the perpendicular direction, where the intensity is only slightly affected,
and no precursor changes are seen in the parallel direction at temperatures below the melting transition. It seems, therefore, that the line broadening, when it occurs, sets in abruptly and is of sufficient magnitude to cause the line to become much broader: its width must increase to a value comparable to or greater than the velocity scan of the spectrometer. This broadening of the absorption in the parallel direction is so large that it cannot be used to gauge the diffusion constant. However, a quantitative estimate can be based on the fractional change in the perpendicular cross section. These changes, amounting to about 20% in each sample at the melting temperature, can be understood as arising from a sampling of the surface parallel signals, due to the distribution of crystallite orientations and finite detector geometry.

Quantitative analysis is based on the theory of section 4. We assume that the state of the film changes from very slow diffusion below the melting temperature to fast liquid-like diffusion above. Then, with the empirical distribution of crystal orientations in Grafoil and Papyex, we obtain from eqs. (16) and (20), the fractional change in average cross section due to melting,

$$\Delta \sigma = \frac{1}{\sigma_0} \left( 1 - \frac{1}{2 \sqrt{\eta}} (1 + 1/\delta \theta) \right). \tag{34}$$

The detector geometry had an angular collimation $\delta \theta \sim 0.05$. We then estimate, according to the observed fractional changes of intensity, $\eta \sim 150$ and $D \approx 10^{-9}$ cm$^2$/s. These values, while satisfying the assumption of fast diffusion, are more characteristic of highly viscous media than of typical bulk fluids or adsorbed monolayer fluids. Normal liquids have diffusion constants of order $10^{-5}$ cm$^2$/s. In a monolayer of methane adsorbed on Papyex graphite at a temperature above its two dimensional critical point $[10]$, Coulomb, Bienfait and Thorel measured a lateral diffusion constant ranging from $10^{-5}$ to $10^{-4}$ cm$^2$/s using the technique of quasi elastic neutron scattering. Two other recent studies $[31, 32]$ of light molecular gases on less well characterized substrates, have yielded values from $10^{-6}$ to $10^{-5}$ cm$^2$/s. These results are too small in number to indicate whether the BIT-graphite system is unusual, or whether there are any unexpected difficulties involved in the Mössbauer technique or its application. At this juncture, we must attribute the particularly low diffusion of BIT on graphite to a combination of intermolecular and molecule-substrate effects. It would be valuable to measure the same system by another technique, e.g. by neutron scattering or nuclear magnetic resonance.

Apart from the question of magnitudes, the semi-quantitative result that the high temperature state of the films is fluid, with fast diffusion along the film plane, is proof that the abrupt transitions are a form of two dimensional melting. This bears on a subject of considerable current interest, involving the nature of long-range order in two dimensional matter.

The gauge of long range order in crystalline matter has for many years been based on the positional regularity of its atomic or molecular units $[33]$. By this gauge long range crystalline order can exist in two dimensional matter only at $T = 0$; at higher temperatures the coherence length is reduced, suggesting that the material might evolve continuously from a solid to a fluid $[34]$. Recently another gauge has been identified, called directional $[35]$ or topological $[36]$ order, and by this gauge a two dimensional crystal can have long range order persisting to finite temperatures. Long range directional order is present in elastic solids; it is the loss of this kind of order that is involved in melting $[37]$. Attempts have been made to calculate the nature of the phase change when a two dimensional elastic solid undergoes a loss of long range topological order $[36, 38]$, but the theory is still in a preliminary state. The present experiments are apparently the first to give direct evidence for changes of fluidity in a first order phase change of adsorbed monolayers. It is of course not possible to specify that the transition is ideally abrupt, but it seems first order to within the experimental resolution of about 2 K temperature width. This width is composed of several factors: the temperature stability of the cryostat, the statistical uncertainty of the intensity data, and the homogeneity of the samples.

It therefore seems that, to within the resolution of the measurement, the BIT monolayer undergoes a two dimensional melting transition analogous to the melting of ordinary bulk crystals, i.e. with abrupt and very large changes in fluidity.

6. Discussion. — This study explores dynamical properties of adsorbed monolayers that are readily measurable by Mössbauer spectroscopy. The measurements have not exhausted the sensitivity of the spectroscopy, for it can be a valuable probe of local fields and chemical changes $[38, 39]$. Our emphasis here is on the dynamical changes in both the perpendicular and surface-parallel directions. Several questions are of quite general importance and can profitably be studied in greater detail and with other systems. The problem of two dimensional melting, which appears to be first order to within experimental resolution, remains important and of considerable current interest. Higher resolution can give a sharper test of its first order nature in both this system and other gases and substrates. Different combinations of gases and substrates are needed to explore the role of substrate structure. Apart from the question of the order of the melting transition, the measurement of surface diffusion coefficients can be important in developing a microscopic view of the nature of the films. It may in addition help to give some insight into the states of the bulk matter, as the films are increased in coverage beyond one or two monolayers.

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