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On the nature of the 2 *D* diffusion of tetramethyltin $\text{Sn}(\text{CH}_3)_4$ on graphite (*)

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Résumé. — La spectroscopie Mössbauer, appliquée aux molécules de $\text{Sn}(\text{CH}_3)_4$ adsorbées sur graphite, permet une estimation du coefficient de diffusion. La dépendance angulaire de la section efficace de résonance permet de déterminer que la diffusion dans le fluide 2 *D* visqueux ($D \sim 10^{-8} \text{ cm}^2/\text{s}$) est du type continu, comme dans les liquides 3 *D* classiques.

Abstract. — Mössbauer measurements of Sn-119 in $\text{Sn}(\text{CH}_3)_4$ molecules adsorbed on graphite yields an estimate of the diffusion coefficient. The angular dependence of the Mössbauer on-resonance cross section makes it possible to determine the nature of the diffusion in the very viscous 2 *D* fluid ($D \sim 10^{-8} \text{ cm}^2/\text{s}$) and shows that it is continuous-like at it is in bulk liquids.

1. Introduction. — The nature of the two dimensional, adsorbed phases have been under current interest since the discovery of Thomy and Duval [1] ten years ago, that the adsorption vapour pressure isotherms have features similar to those of bulk matter. The phases were named solid, liquid and gas, in analogy with the three dimensional properties. Since then the 2 *D* solid has attracted an extensive amount of experimental and theoretical attention. Registry-non registry transitions, polymorphism and possible existence of directional, rather than positional order which were attributed to these solids, indicate some of the intrinsic properties of two dimensional adsorbed phases. Less attention was devoted to the 2 *D* fluids on surfaces. The transition into this state was extensively studied by specific heat measurements [2], n.m.r. [3], neutrons [4] and Mössbauer [5-9] spectroscopy.

The Mössbauer spectroscopy has already been used to study diffusion in bulk glasses and super-cooled liquids [10]; this technique is not suitable for typical 3 *D* liquids where the diffusion rate is too high for detectable recoilless resonance to occur. This is not necessarily so for the 2 *D* case.

The question of the detailed nature of the molecular motion in bulk liquids has been increasingly clarified by both experiments and calculations in the last decade. It was necessary to determine whether the molecules in a liquid diffuse by infrequent large jumps or by frequent small motions (continuous diffusion). A few years ago, it was demonstrated that the diffusion in bulk liquids is of a continuous nature [10].

In molecular films, however, the effective line broadening due to diffusion can be less. For aligned substrates, such as Papyex or Grafoil, the diffusion in the film plane can be detected. The effect of the diffusion on the cross section can be effectively attenuated by geometrical factors when observed in other directions. This enables the Mössbauer technique to probe the mobile states of the films and to observe mobility changes. The first demonstration of this technique was published recently [5, 6, 8]; the preliminary results encourage a further pursuit of this problem.

Recently we have been concerned with the problem of large molecules adsorbed on graphite in the form of Papyex, and particularly the 2 *D* solid, which probably may be non-registered with the substrate due to the relatively large molecular size (the $\text{Sn}(\text{CH}_3)_4$, has a

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diameter of $\sim 7 \text{ \AA}$) and in the fluid into which it transforms. This liquid is found to be very viscous : if the mobility mechanism is due to diffusion, the diffusion coefficient is $\sim 10^{-8} \text{ cm}^2/\text{s}$ as compared to $10^{-5} \text{ cm}^2/\text{s}$ in *regular* liquids. The results of these work will be published elsewhere. In this note, we discuss the nature of the molecular motion in the 2 *D* fluid of the molten 2 *D* solid of tetramethyltin on Papyex, as observed by Mössbauer spectroscopy. We first summarize the existing theoretical situation in order to show how the results can be applied to our problem.

2. Background. — In a recent report, we discuss in some detail the Mössbauer cross section of mono- and submonolayer films, particularly the effect of the diffusion. Based on Singwi and Sjölander's work on diffusion in bulks [11], we suggested a solution that will describe the 2 *D* classical liquid [6] :

$$F_s(\mathbf{r}, t) = (2\pi r)^{-1} (\pi D t)^{-1/2} \exp(-r^2/4Dt),$$

where $\mathbf{r}$ is the displacement vector in the plane of the surface, $F_s(\mathbf{r}, t)$ is the classical self diffusion function. Substituting in the general expression for the resonant cross section σ_{res} (eq. (37), ref. [11]), we obtain that for two dimensions

$$\sigma_{\text{res}} = \frac{\sigma_0}{2} \exp \left[-\frac{\hbar^2 k^2}{8 m k_B T} \right] (1 + \eta \sin^2 \theta)^{-1/2}, \quad (1)$$

where $\eta = 2 \hbar D k^2 / \Gamma$. D (diffusion coefficient) is the mean square displacement per unit time and its determination may depend on the lifetime $2 \hbar / \Gamma$ of the gamma ray, $k = E\gamma / \hbar c$ is the wavevector of the gamma rays, Γ is the natural linewidth. θ is the angle of $\mathbf{k}$ with respect to the normal to the surface film.

It can be seen therefore, that unlike bulk liquids [11], for surface films there is an angular dependence. If $\eta \ll 1$, the diffusion has little effect on the linewidth and cross section, while for $\eta \gg 1$, the effects of diffusion can be changed from the fast diffusion range to the slow, as θ is varied from $\pi/2$ to 0. Equation (1) assumes a continuous liquid-type diffusion.

The diffusion of atoms in a crystalline solid is characteristically a hopping motion ; an atom resides in a site, then jumps to the new site. We have applied arguments similar to those of reference [11], for our 2 *D* case : assuming an isotropic surface and jumps of equal lengths r_0 , τ_0 is the mean residence time on a site, one can show that for the fast diffusion range [6] ($\eta \gg 1$),

$$\sigma_{\text{res}} = \frac{\sigma_0 \Gamma}{4} \exp \left[-\frac{\hbar^2 k^2}{8 m k_B T} \right] \frac{1}{\Gamma + \frac{4 \hbar}{\tau_0} \left| \sin \left(\frac{k r_0}{2} \sin \theta \right) \right|}. \quad (2)$$

Under certain conditions, where $k r_0 \ll 1$ (small jump distances), (1) and (2) are similar. Actually, for our Sn-119, 24 keV, $\frac{k r_0}{2} \sim 25$ (r_0 was chosen as an average jump distance on the graphite mesh, such as in a $\sqrt{3}$ structure, which is $4.26 \text{ \AA}$; but this is just an estimate ; any other reasonable choice keeps the result within the same order of magnitude). Thus, from the angular dependence of the on-resonance cross section, we should be able to tell the difference between (1) and (2). The net result of (2) is a cross section with a narrower peak near $\theta = 0$. This type of angular dependence due to stepwise diffusion is different from that predicted by (1) for liquid-like diffusion.

3. Technique, results and comments. — Most of the technical details concerning Mössbauer spectroscopy applied to adsorbed films are described in a recent report [6]. We have shown above that in order to distinguish between stepwise and continuous diffusion, an angular dependence measurement of the resonance cross section is necessary. A special cell was constructed (Fig. 1) which enables measurements

Fig. 1. — The Mössbauer cell for measurements of the Mössbauer cross section angular dependence as a function of temperature. (a) cooling cavity; (b) heater; (c) thermometer (GaAs); (d) Mylar windows; (e) charging tube for adsorption gas on the Papyex stack (f). The Papyex sheets were cut with a cylindrical shape to obtain an atomic absorption of the gamma rays as close as possible to each other for various angles. The graphite *c*-axis is, on average, perpendicular to the Papyex sheets.

with the gamma k -vector in various directions relative to the plane of the adsorbing Papyex sheets to be made. The cavity of the cell having several through windows. The adsorbing substrate was composed of several Papyex sheets each 1 mm thick giving a total weight of 15 g with $21 \text{ cm}^2/\text{g}$ adsorbing area of primarily basal plane exposure. The adsorbed material (0.8 of a monolayer) was sufficient to yield a good Mössbauer single line [9] with a Sn-119 in calcium stannate gamma source. The preferential orientation of the planes was parallel to the plane of the cylindrical shape, 25 mm diameter and 30 mm long. This shape was necessary to avoid different atomic absorption of the 24 keV gammas along various directions. The stack of foils was aligned in the cell cavity with the planes vertical so that rotation about a vertical axis enabled measurements to be made for few chosen directions. The size of the windows, together with the aid of a collimator enabled the two angles different by $\sim 10^\circ$ to be aligned through each window. In this way, there are experimental points at $\theta = 0^\circ$ and $\theta = 90^\circ$ and at intermediate angles.

The spectra were taken along different directions at a temperature above the 2 D melting of the tetramethyltin ($\sim 85 \text{ K}$). The results are shown in figure 2.

In order to determine the character of motion on the molten 2 D phase, it is necessary to fit either equation (1) (diffusional) or equation (2) (stepwise) to the experimental points. σ_{eff} in each case is the effect normalized in such a way that $\sigma_{\text{eff}} = 1$ at $\theta = 0^\circ$. Thus σ_{eff} measures the relative change of the intensity with angle : a fit was done by changing D (or τ_0) in steps.

Some of the results of this fit are illustrated in figure 2. The inset magnifies a region of the curves to make the discrimination easier.

From the results of this fit, it is clear that equation (1) is the most probable, with $D \sim 5.5 \times 10^{-8} \text{ cm}^2/\text{s}$. One cannot ignore, however, that the fits for equation (2) are also not too far away from the experimental points (see curve *c*). But this is for residence times of around 4×10^{-11} seconds, which is extremely small compared to the τ_0 values for typical solids [11] (of the order of $\sim 10^{-6} \text{ s}$). It means that within the nuclear lifetime ($\sim 10^{-8} \text{ s}$ which is our time of measurement) the molecule spends practically no time at the *site*, and therefore it represents practically continuous like diffusion and as such does not really contradict the result of the fit of equation (1). The value for D ($\sim (5.5 \pm 1.5) \cdot 10^{-8} \text{ cm}^2/\text{s}$) obtained from this fit agrees reasonably well with a preliminary value obtained by inelastic neutron scattering [12], and with a Mössbauer result at T_m [12] which both yield $(3 \pm 1) \cdot 10^{-8} \text{ cm}^2/\text{s}$.

It should be considered that practical substrates have some surface misorientation ; there are regions which are planar on a scale which is large compared to

Fig. 2. — The effective cross section *versus* the direction of the gamma rays relative to the normal to the surface. σ_{eff} in both equations (1) and (2) were normalized to yield 1 at $\theta = 0^\circ$. The inset is the expanded central part of $\sigma_{\text{eff}}(\theta)$ to demonstrate the closeness of fits by equations (1) and (2). *a*) equation (2), $\tau_0 = 4.6 \times 10^{-11} \text{ s}$; *b*) equation (1), $D \simeq 5.5 \times 10^{-8} \text{ cm}^2/\text{s}$; *c*) equation (2), $\tau_0 = 4.0 \times 10^{-11} \text{ s}$; *d*) equation (2), $\tau_0 = 2.0 \times 10^{-11} \text{ s}$; τ_0 is the residence time at a site (see text).

the diffusion length. Equation (1) is valid for such cases. One must calculate the average cross section if there are also misoriented regions present. For the Papyex used in this experiment, there is some misorientation with a narrow peak ($\pm 15^\circ$) [13]. Experimental results for $\text{Sn}(\text{CH}_3)_4$ in directions parallel and perpendicular to the surface show a strong θ dependence. The strong reduction of the resonance cross section observed for $\theta = \pi/2$ is not visible for $\theta = 0$. We therefore used the expressions for aligned films. This choice is justified from quantitative calculations of the expected reduction in the average cross section for Papyex as a function of θ and various coefficients of diffusion [12]. The results indicate that for diffusions slower than $\sim 10^{-7} \text{ cm}^2/\text{s}$ the Grafoil or Papyex are practically aligned.

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