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The present equations permit a theoretically sound extension down below the critical temperature into the unsaturated vapor isothermals, so long as the volume is large compared with that of the liquid phase of the given assembly. It also permits an extension up to the critical temperature of the saturated vapor pressure curves, which is, however, merely a formal extension of equations which have been proved only under

the limitation that the condensed phase shall contain a negligible proportion of the molecules of the assembly.

These restrictions are inherent in the assumptions made at the beginning of the work, and there seems no way of removing them if the dissociation method is to retain its advantage of simplicity over that of the more completely rigorous treatment of Mayer.^{3a, b}

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Changes of Phase and Transformations of Higher Order in Monolayers

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The gaseous, liquid, mesomorphous and solid states in monolayers are defined and their close connection with the corresponding states in three dimensions rigorously established. This involves a new treatment of the two-dimensional liquid and of its transformation to the mesomorphous state. The properties of the three-dimensional vitreous state of fatty substances are shown to be particularly important in connection with the behavior of monolayers. The different critical and transformation temperatures are also defined and their significance explained. From this is derived a systematic classification of the different types of isotherms observed. By determining the variations of the compressibility, viscosity and apparent dipole moment with change of area, higher order transformations are detected in monolayers. These transformations occur at the same areas as those at which ordinary phase transformations occur at lower temperatures.

THE aim of this paper is to establish a general correlation between all the transformation phenomena observed in surface films and to show that they correspond closely to the transformations found with the same substances in bulk. This enables us to set up a rigorously defined nomenclature without the implication of any vaguely justified assumption. *Critical temperatures* and a *triple point* will be defined thus permitting us to arrange the different states in which a film can exist, when its temperature and pressure are fixed, in a systematic classification. For this purpose some new experimental data are included together with a new interpretation of some of the published experiments.†

Both from the theoretical and experimental point of view, transformations in two dimensions

are more readily studied than in three dimensions. In two dimensions, by relatively simple means, pressures which in three dimensions would correspond to some hundreds of atmospheres or alternatively to a few tenths of a millimeter of mercury can be attained. Likewise, molecular packing, molecular interaction, questions of order and disorder, are much simpler in a two-dimensional system than in a three-dimensional.

Besides the ordinary phase changes, transformations of a higher order are found in monolayers. These are detected by sharp discontinuities occurring simultaneously in three different physical properties: compressibility, apparent dipole moment and especially the surface viscosity. Accurate determination of variations in the compressibility and in the apparent dipole moment was made possible by the use of a method of automatic and continuous registration of both pressure and potential isotherms. A considerable improvement could thus be obtained

* Rockefeller Foundation Fellow 1938-39.

† References will be given only for typical experiments. For a general survey and bibliography see: E. K. Rideal, *Surface Chemistry* and N. K. Adam, *The Physics and Chemistry of Surfaces*.

in establishing the usual phase change discontinuities. The automatic registering apparatus has been previously described.¹ Contrary to what might be thought at first sight, there is less danger of recording metastable states by this method than by the ordinary methods. In the ordinary method, when the barrier is moved from one point to another, the film is compressed relatively quickly; while in the recording apparatus, the movement is continuous but slow enough to maintain the film continuously in equilibrium. On the other hand, the determination of the pressure at each point does not involve appreciable periods of time during which the film may dissolve or collapse. Records have been made at different speeds and it has been found that, provided the speed be not too great, the curves are identical.

COMPRESSIBILITY

Since every isotherm is recorded with the same film, the relative error in the surface concentration is kept constant all along the curve. This gives a much sharper determination of the shape of the curve (i.e., the slope at every point) and shows up any singularities. To plot the variations of the compressibility against the area per molecule A , values of $dA/d\pi$ are determined² and inserted in the expression:

$$K = -dA/d\pi.$$

The sharpness of the registered line permits us to make a graphical evaluation of the tangent at different points to within less than one degree. For angles between 30° and 60°, this gives an error of less than 5 percent. To keep between these limits the sensitivity of the recording instrument is adjusted to the part of the isotherm under examination and different initial concentrations are employed so that the curve is more or less tilted on the axis.

APPARENT DIPOLE MOMENT

The same remarks about the sharpness of the

¹ D. G. Dervichian, J. de phys. et rad. [7] 6, 221 and 427 (1935); Ann. de physique [11] 8, 361 (1937).

² The notation π for surface pressure will be used following E. A. Guggenheim (*Thermodynamics*, p. 179). The ordinarily used F notation may bring confusion with that of the free energy. Moreover, it stands as an abbreviation of "force," when actually, as is well known, it represents a two-dimensional pressure.

curve are also applicable to registered isotherm of the surface potentials: singularities can be detected on the ΔV curve. It is well known³ that values of the dipole moment $\mu = 4\pi n$, calculated from the potential fall ΔV , are very different from those found by other methods. We consider it here as an *apparent* moment corresponding to a *fictive* Helmholtz double layer which is not formed solely by the whole of the dipole moments of the film.

While ΔV increases generally with the surface concentration, μ is not necessarily constant and its variation shows transition points. The detection of these transition points is one of the aims of the present work.

SURFACE VISCOSITY

It has been previously shown⁴ that the flow of a monolayer through a narrow canal reveals a true viscosity of the film which varies with its nature and state. In this paper variations of this viscosity at different surface concentrations (i.e., different pressures) of the same film are described. The film flows under a constant and accurately measured difference of pressure of less than 0.5 dyne/cm and the apparatus is so devised that both the high and low pressures are kept constant during the flow.⁵ The determination of the viscosity in the layer, from the rate of flow implies some assumptions which are far from being unquestionable. We are here more interested in singularities in variations than in absolute values, so only the actually measured *rates of flow* are quoted. Moreover, for all determinations, the same canal has been used, thus making all the results comparable. The results are reproducible to within 2 to 3 percent.

THERMODYNAMICAL DEFINITION OF TRANSFORMATIONS OF DIFFERENT ORDER

The conception of transformations of different orders, emphasized by P. Ehrenfest,⁶ generalizes

³ See remarks by Schulman and Rideal, Proc. Roy. Soc. A130, 259 (1931) and by A. Frumkin, Zeits. f. physik. Chemie 109, 34 (1924).

⁴ Dervichian and Joly, Comptes rendus 204, 1318 (1937); M. Joly, J. de phys. [7] 8, 471 (1937); Dervichian and Joly, in press and Nature 141, 975 (1938).

⁵ All the viscosity work was carried out by M. Joly. For full details see an article to be published in this journal.

⁶ P. Ehrenfest, Proc. K. Akad. Amsterdam 36, 115 (1933).

the definition of such points as λ or Curie points. The various transformation points are considered as corresponding to discontinuities of the derivatives of different order of a thermodynamical function. For the surface phenomena, here considered, we have to introduce, in the definition of this function, a term corresponding to the surface energy. If γ is the surface tension of the surface covered by a film and γ_0 that of the clean surface, the work done by an infinitesimal displacement of the barrier, which changes each of the two areas by dA and $-dA$, respectively, is

$$dw^s = (\gamma - \gamma_0)dA. \quad (1)$$

Introducing the surface pressure, $\pi = \gamma_0 - \gamma$, the relation (1) takes the form

$$dw^s = -\pi dA \quad (1')$$

similar to the work in the bulk

$$dw^v = -PdV. \quad (2)$$

If S represents the total entropy (surface and bulk) of the system, the variation of the total energy is defined by:

$$dE = TdS - PdV - \pi dA. \quad (3)$$

When T , P and π are considered as the independent variables, we adopt, as thermodynamical function, the thermodynamic potential G of Gibbs, in which we introduce a term corresponding to the surface energy, analogous to the term PV :

$$G = F + PV + \pi A,$$

where F is the free energy, $F = E - TS$. This gives with (3):

$$G = E - TS + PV + \pi A$$

and

$$dG = -SdT + VdP + Ad\pi, \quad (4)$$

which enables us to calculate the successive partial derivatives:

$$(\partial G / \partial \pi)_{P, T} = A, \quad (5)$$

$$(\partial^2 G / \partial \pi^2)_{P, T} = \partial A / \partial \pi. \quad (6)$$

An ordinary change of state will be called a *transformation of the first order*, since it is characterized by a discontinuity in the area A and consequently corresponds to a discontinuity in the first derivative of G . Likewise a transforma-

tion in which A does not undergo any sudden variation, but in which the compressibility

$$K = -\partial A / \partial \pi \quad (7)$$

shows a discontinuity, will be a *transformation of the second order*, since according to (7) and (6) it corresponds to a discontinuity in the second derivative of G . In the same way, a transformation of the third order will be characterized by a discontinuity in the third derivative of G (with the exclusion of the two preceding derivatives), that is in $\partial K / \partial \pi$.⁷

Experimental material

Typical substances studied in monolayers are the long chain acids and alcohols or their derivatives: esters, triglycerides, amines, amides, etc. It is well known that for members of a homologous series, the melting point (and, in general, the various other transformation temperatures) increase with the chain length. As will be seen, the same variation is found in the changes of state of the same substances spread in monolayers. Hence, to study the different states in monolayers, we may either examine the same substance over a large range of temperature, or else examine the different members of the series at the same temperature. But the available temperature range is limited both by the freezing point of the substrate and by the fact that with present technique it is impossible to make precise measurements above 45–50°. So, by examining the various members of the series throughout that range, we obtain overlapping results which enable us to follow all the successive changes of state that a substance in monolayer form can undergo: from melting of the solid up to and beyond the critical temperature of liquefaction. We gain supplementary information by examining at a given temperature the changes of state that are produced by changes of the surface pressure.

The different states in films

H. Devaux was one of the first to point out that, even when they are one molecule thick,

⁷ Likewise, discontinuities in one or other of the successive partial derivatives:

$(\partial G / \partial T)_{P, \pi} = -S = -q/T$ and $(\partial^2 G / \partial T^2)_{P, \pi} = C_P/T$ correspond, the first, to an ordinary transformation by change of temperature and the second, to a real Curie point.

solids and liquids maintain their mechanical properties. He thought that by varying the temperature over sufficient range, a given substance, spread in a monolayer, would show all the different states of matter. This is now well established. Monolayers may exist in the solid, mesomorphous, liquid and gaseous states.

The existence of gaseous films was predicted by I. Langmuir and the first systematic investigation on this state made by Adam and Jessop.⁸ Different suggestions have been given⁹ to explain the phase which is generally known as "liquid expanded." It will be shown that this is the corresponding state of the ordinary three-dimensional liquid. An intermediate state between the liquid and the solid, has been called "liquid condensed" by Adam. It was pointed out by Lyons and Rideal,¹⁰ that this was the two-dimensional analog of the liquid crystal or smectic state of bulk matter. New evidence will be given to confirm this point of view. The word "mesomorphous," which implies no definite structure, will be used to designate this state of films. Before reaching the liquid state, the mesomorphous film undergoes a transformation which was first investigated by H. Labrousse.¹¹ It will be shown that this behavior is similar to that in three dimensions in the transition from anisotropic liquid crystal to the isotropic liquid state. The state of the film during this "Labrousse's transformation" will be termed "expanded mesomorphous." In the solid state, the *A*, *B*, *C*, crystalline varieties of the fatty acids, and the stable and unstable forms of triglycerides—known in three dimensions—are found in monolayers.¹² They give us some information on the probable arrangement of the molecules on the surface.

Existence of different points of transformation of higher order

It will be seen that *areas corresponding to ordinary phase changes, are found as points of discontinuity of higher order in those phases which*

⁸ Adam and Jessop, Proc. Roy. Soc. **A110**, 423 (1926).

⁹ Adam and Jessop, Proc. Roy. Soc. **A112**, 364 (1926); D. G. Dervichian, Comptes rendus **194**, 2129 (1932); I. Langmuir, J. Chem. Phys. **1**, 756 (1933).

¹⁰ Lyons and Rideal, Proc. Camb. Phil. Soc. **26**, 419 (1930).

¹¹ H. Labrousse, Ann. de Phys. [9] **14**, 164 (1920).

¹² D. G. Dervichian, Comptes rendus **199**, 347 (1934) and Ann. de physique [11] **8**, 361 (1937).

exist at higher temperatures. Thus 20.5Å^2 being the sublimation point in the solid state is found as a point of second order in the mesomorphous state. It is interesting to note that the triple point $38\text{--}39\text{Å}^2$ persists in all liquid and highly compressed gaseous films in the form of discontinuities in the compressibility, viscosity and moment when that area per chain is reached. A list of these characteristic areas is given at the end of the paper.

The different critical and transformation temperatures

T_{cl} .—In their study of the transition from the gaseous to the condensed states, Adam and Jessop⁸ considered critical phenomena analogous to the three dimensional. We shall define for every substance a *critical temperature of liquefaction* T_{cl} above which the film does not undergo liquefaction by compression.

T_{cc} .—Adam and Jessop⁹ have established a whole series of isotherms for the transition by compression from the liquid to the condensed (expanded mesomorphous) state. Above a certain temperature, this transition does not occur and the film remains liquid up to the collapse pressure. We shall term this point the *critical temperature of crystallization*: T_{cc} .

T_s .—The solid state is well defined. The area per chain, under the pressure of the saturated vapor, remains constant and equal to *ca.* 20.5Å^2 up to a temperature T_s . Then the mesomorphous state appears with an area of *ca.* 23.5Å^2 per chain. This is invariable up to another temperature.

T_m .—Where the expansion of the mesomor-

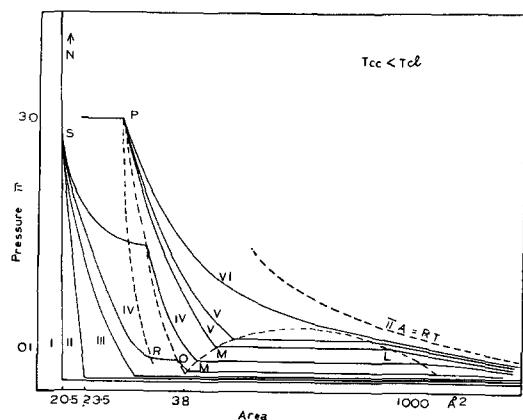


FIG. 1. Possible forms of isotherms when $T_{cc} < T_{cl}$.

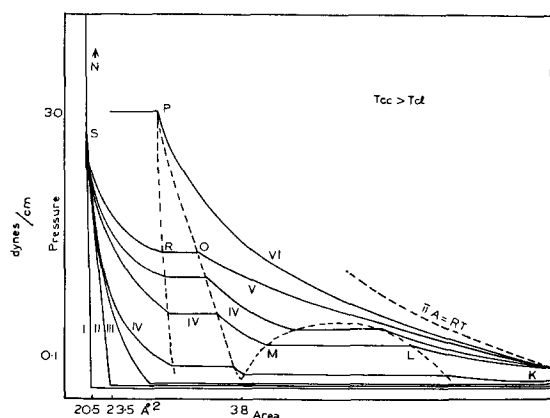


FIG. 2. Possible forms of isotherms when $T_{cc} > T_{cl}$.

phous state (Labrouste's transformation) commences.

T_l .—This transformation terminates at T_l , which is the real *melting point*, or temperature of appearance of the liquid state under the pressure of the saturated vapor. This will be defined as a *triple point* and the corresponding area (under the pressure of the vapor) is 38–39 Å² per chain. This plays an important rôle in the transformations of higher order.

We shall refer later to the three-dimensional correspondence and meaning of T_l and T_{cc} . The “half expansion temperature”¹³ introduced by Adam, has an arbitrary definition and has no physical significance.

Classification of the different types of isotherms

For a given substance, the critical liquefaction temperature is not necessarily higher than the critical crystallization temperature. We shall consider the two cases in a general classification of the different types of isotherms. In Figs. 1 and 2 are depicted schematically all the possible forms of isotherms and their derivation according as T_{cc} is below or above T_{cl} . In order to represent on the same graph the complete development of the films, the pressure scale is larger at the bottom than at the top of the figure. Likewise, the area scale is extended on the right side. On the abscissae are indicated the characteristic areas per chain (under the pressure of the saturated vapor) of the different states and crystalline forms.

¹³ It is defined as the temperature for which the area, under a pressure of 1.5 dynes/cm, is half-way between the condensed and the expanded states.

1°. $-T_{cc} < T_{cl}$.—Fig. 1 is applicable to substances in which the film always begins to liquefy before undergoing solidification by compression.

2°. $T_{cc} > T_{cl}$.—Fig. 2 is applicable to films which may still solidify by compression even when it can no longer liquefy.

We note that both types of isotherms have the same form at low temperature and even after the appearance of the liquid state; but they differ markedly at relatively higher temperatures. For the second type (Fig. 2), direct transition from the solid or mesomorphous phase to the gaseous may occur. This case must not be confused with the one where there is sublimation (lowest isotherms of both Fig. 1 and 2). In the later case, condensation takes place from a very dilute gas, while in the case under consideration the transition begins from a very concentrated gas occupying an area smaller than its “critical area.”¹⁴ Films in this state have been called by Adam “vapor expanded films” by analogy to the liquid films which he calls “liquid expanded films.”

We shall now define successively the gaseous, solid, liquid and mesomorphous states, and particularly their transformation points (ordinary and higher order). An attempt will be made to explain their significance.

The two-dimensional gaseous state and condensation

From the outset of the work on surface films, a comparison was made between two- and three-dimensional gases, but we shall not dwell on the historical aspects.

Adam and Jessop established a series of isotherms, now classical, of a homologous series of acids. The general form of these curves (Fig. 1, V) recall the ordinary gas isotherms. The point M (molecular area of 20 to 100 Å²) is the beginning of a transition horizontal part, at relatively low but constant pressure (0.2 dyne/cm for

¹⁴ Adam and Jessop [Proc. Roy. Soc. A112, 362 (1936)] have established the isotherm at 17° of ethyl palmitate up to about 2000 Å². This reveals, instead of a transition to liquefaction, a strong inflection around 150–200 Å², as if the film was near its critical temperature of liquefaction. While at 55 Å² and at a pressure of only 3.5 dynes/cm there appears a transition to crystallization. Films of methyl-11-ceto-stearate are gaseous up to a molecular area of 120 Å², then condense into a solid phase, along a horizontal transition flat, at a pressure of 5 dynes/cm. This is another example for the case illustrated by Fig. 2. (See D. G. Dervichian, Ann. de physique, reference 1.)

myristic acid), which extends to some hundreds or thousands \AA^2 (ca. 900 for myristic acid). Then, beginning from L , the pressure π decreases gradually along LK tending asymptotically towards the $\pi A = RT$ hyperbola. If the areas and pressures are expressed in c.g.s. units, the constant R is the same as the three-dimensional perfect-gas constant; T is the absolute temperature.¹⁵

Adam and Jessop extended their measurements to about 5000\AA^2 per molecule. J. Guastalla¹⁶ using oleic acid was able to reach extensions up to $30,000\text{\AA}^2$ (area at $L=5000$) and found that the isotherm appeared to coincide with the ideal gas hyperbola. More recently Guastalla¹⁷ has again taken up the question of measurements at very low surface concentrations with an apparatus based on a new principle, which enables him to measure easily surface pressures of the order of $1/1000$ of a dyne/cm.¹⁸ He has thus been able to reach areas of more than $100,000\text{\AA}^2$. At this concentration, the mean intermolecular distance corresponds to that in a solution of 10^{-4} or 10^{-5} normal, or to a gas under the pressure of $\frac{1}{2}$ -mm of mercury. Before reaching this value, the isotherm practically follows the $\pi A = RT$ hyperbola.

With a film of methyl-11-ceto-stearate, an isotherm was found¹⁹ which follows the hyperbola from 1500\AA^2 .

It is generally accepted that the LK part of the isotherm corresponds to the gaseous state. According to the case, this gas, or vapor, gives by condensation a liquid phase ($T > T_l$, oleic acid and tricaprinn at room temperature, myristic acid above 5° , trimyristin above 30° , Fig. 1 or 2, IV and V) a mesomorphous phase ($T_s < T < T_m$, palmitic or stearic acid on dilute HCl at room temperature, Fig. 1 or 2, II and III), or a solid phase ($T < T_s$, tripalmitin or stearic acid on distilled water at room temperature, trimyristin

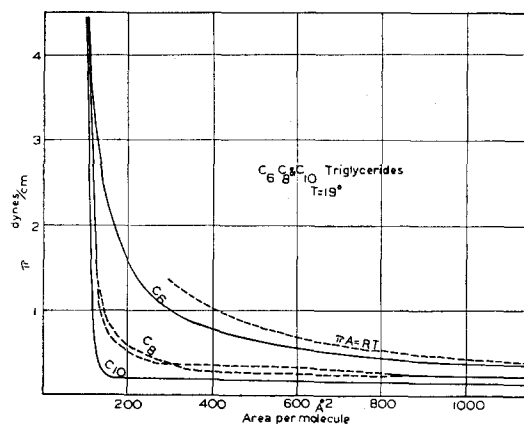


FIG. 3. Isotherms (π - A) of the C_6 , C_8 and C_{10} triglycerides.

below 21° , Fig. 1 or 2, I). In other words, the reverse transformation would be a *vaporization* or a *sublimation*. Whatever be the assumption as to the orientation of the molecules, we must have, all along the LM flat part of the curve, two phases in coexistence, one growing at the expense of the other. Surface potential measurements show that the film is inhomogeneous in this region, and it has been proved that the condensed phase (liquid or solid) forms flat aggregates whose dimensions may attain some centimeters.²⁰

Films not liquefying by compression ($T > T_{cl}$).— Films may give isotherms without a transition from the vapor (Fig. 1, VI, Fig. 2, V and VI). A typical case is given by the C_6 triglyceride: tricaprinn. This is shown in Fig. 3, upper isotherm. There is no discontinuity in the isotherm. Likewise the surface potential curve decreases quite regularly. The two other curves refer to the two higher terms of the series: C_8 (tricaprylin) and C_{10} (tricaprinn). C_{10} gives a transition flat between 120 and 4000\AA^2 ; as for C_8 , the results are quite variable in the middle range of concentration, presenting all the characters of an unstable region of transition. The variations of temperature which have been used were not sufficient to produce any state of equilibrium. It is to be noted that such large molecules can easily form metastable films; this is also noticed in solidification from the liquid.²¹

¹⁵ This was observed by Langmuir for the adsorbed soluble substances and foreseen by him for the insoluble very dilute films. The kinetic interpretation may be found in Adam and Jessop's original paper, reference 8. We are not concerned here with the actual position of the molecules in the gaseous state (lying flat or not). See the discussion in Adam's *The Physics and Chemistry of Surfaces*.

¹⁶ J. Guastalla, *Comptes rendus* **189**, 241 (1929).

¹⁷ J. Guastalla, *Comptes rendus* **206**, 993 (1938) and *J. de phys. et rad.* (1939).

¹⁸ The chief feature of the technique is the great care taken to clean the surface. This is always incomplete in the ordinary method of scraping the surface with movable barriers.

¹⁹ D. G. Dervichian, *Ann. de physique* [11] **8**, 405 (1937).

²⁰ Adam and Harding, *Proc. Roy. Soc.* **A138**, 411 (1932); Schulman and Rideal, *Proc. Roy. Soc.* **A138**, 430 (1932); D. G. Dervichian, reference 1.

²¹ According to Adam and Jessop's isotherms, lauric acid (C_{12}) seems to be in the neighborhood of its critical tem-

Critical temperature of liquefaction

As will be seen, the range of temperature, limited by experimental conditions, often includes different points of transformation of the condensed phase of the same substance; but to pass the critical point of liquefaction requires a much wider range, and it has not yet been possible to plot, for the same substance, isotherms situated on each side of the critical point. But in consequence of the fact that the temperatures of the different points of transformation increase with the length of the chain we can consider the different isotherms of Fig. 3 as if belonging to the same substance, investigated at three different temperatures. We may state that every substance, when spread as a monolayer, has a critical temperature of liquefaction and that, at room temperature, tricaprylin is in the neighborhood of its critical temperature, tricaproin distinctly above, and tricaprin, and all the higher homologues, below.

Transformation of higher order in gaseous films

While the isotherm of tricaproin shows no discontinuity, the compressibility, the dipole

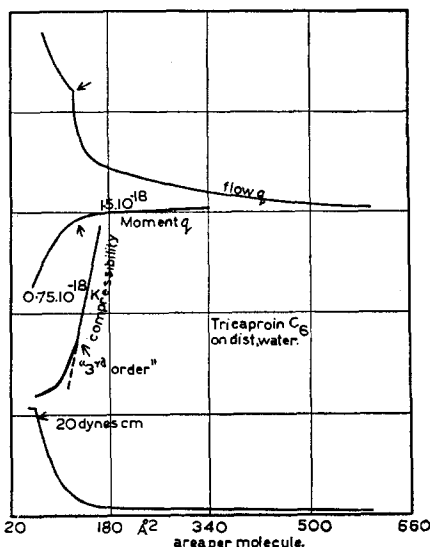


FIG. 4. Discontinuity of higher order in a highly compressed gaseous film (tricaproin C_6). There is a very marked kink in the fluidity curve at about $115-120\text{\AA}^2$. The compressibility shows only an inflection at the same area; this would show a discontinuity on the dK/dA curve. According to definition, this corresponds to a discontinuity of the third order. There would also be a break in the derivative $d\mu/dA$ of μ .

perature. But, as this substance is slightly soluble, the curve is incomplete.

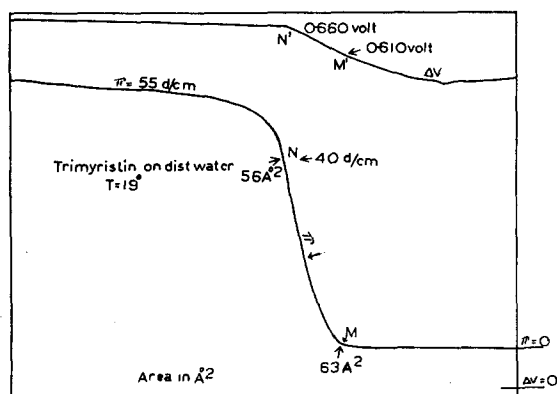


FIG. 5. Registered isotherm and ΔV curves of a solid film: Trimyristin (C_{14}) on distilled water at 19° . By placing a ruler along the curve one can easily see the marked changes of slope.

moment and especially the viscosity (actually the rate of flow) reveal a point of transformation at about $115-120\text{\AA}^2$ as may be seen on Fig. 4. Tricaprylin behaves in the same way. The significance of this $115-120$ point will be given later. Methyl-11-ceto-stearate and ethyl-11-oxy-stearate also show very distinct points of transformation of high order in the gaseous part of their isotherms. These are due to the presence of the supplementary polar groups of the molecules.

The two-dimensional solid state

A monolayer of trimyristin at room temperature is a representative solid monolayer. Besides cohesion, it shows another characteristic of solids: rigidity.²² Fig. 5 reproduces the registered isotherm of this monolayer spread on distilled water at 19° . At any temperature below 21° , the same diagram is obtained. Discontinuities are seen on both the pressure (π) and the surface potential (ΔV) isotherms. The pressure curve is an isotherm of sublimation. The area at M is the area occupied by a molecule in the solid under its saturated vapor pressure. We find for this molecular area, values between 62.5 and 63.5 (average of 63\AA^2). By further compression, the pressure rises rapidly, then at a certain minimum area the film collapses. With trimyristin, there is a sudden discontinuity only on the potential curve at N' , the isotherm showing only an inflection starting at N , whence the slope decreases

²² For the study of the rigidity see: Mouquin and Rideal, Proc. Roy. Soc. **A114**, 690 (1927); for the resistance to shearing, see: M. Joly, J. de phys. et rad. [7] **8**, 471 (1937).

with the appearance of the three-dimensional phase. This point (N or N') corresponds to a minimum area of 55–56Å². With the C₁₆ and C₁₈ triglycerides, the same curve and areas of 63 and 56Å² are found. These areas are independent of the molecular volume.

Solid films can be obtained by compression of a fluid film, we are concerned in this paragraph only with those films which are already solid under their saturated vapor pressure. At room temperature, normal fatty acids give such films only when the number of carbon atoms is at least 18. For the C₁₈, C₂₀ and C₂₂ acids, the area at the sublimation point M is very nearly 20.5Å² and remains constant over large range of temperature as long as the film is solid. The minimum area is indicated in these cases by a sudden break, the isotherm showing a very sharp point after which the pressure falls (Fig. 14). This occurs at *ca.* 18.5Å². It is remarkable that the minimum area of 55–56Å² found for the triglycerides is equal to 3×18.5 .

Discontinuities of second-order in solids

The isotherms of the solid triglycerides show two changes of slope, which correspond to sudden changes in the compressibility. It is difficult to find evidence for any corresponding singularities in the dipole moment. But, on the trimyristin potential curve, recorded at 19°, two breaks are noticed. These breaks as well as the change in compressibility occur at 57.5Å² ($= 3 \times 19.2$) and 60.6 ($= 3 \times 20.2$). The solid fatty acids show the same discontinuities at about 19.3Å² and 20.3Å².

DISCUSSION ON DATA GIVEN BY X-RAY ANALYSIS OF FATTY SUBSTANCES

Fatty acids

X-ray crystal analysis reveals that, according to conditions of solidification, a fatty acid may show three or four different values for the long spacing. These correspond to one of the A , B , C or D crystalline varieties.²³ In each of these polymorphous varieties, the spacing varies linearly with the number of carbon atoms, and the slope of the variation enables us to calculate the angle of tilt of the molecule on the plane of

stratification. Whatever the chain length, this angle is the same and has values of about 70°, 60° or 50°²⁴ for the A , B , or C form, respectively. Thus the different intervals found with the same acid correspond to the different "heights" of the molecule, which has a constant length but is more or less tilted. A consequence of this is that if we calculate the area available per molecule on each plane of stratification²⁵ (ratio of the molecular volume by the height), the same values of 19.5, 20.5 and 23–24Å² are found for the A , B and C varieties of all the acids from C₁₀ to C₂₆. We can consider these three values of the molecular area as the horizontal section of a more and more inclined molecule, the cross section remaining constant. One finds 18.5Å² for this cross section; that is the area which the molecule would have if it was completely erect. Müller has studied a single crystal of stearic acid and found the following dimensions of the unit cell:

$$a = 5.546, \quad b = 7.381, \quad c = 48.84.$$

a and b are the sides of the rectangular base. The average number of molecules for each unit rectangle being 2 (1 central + $\frac{1}{4}$ of each of the four corners), the area per molecule is $ab/2 = 20.5\text{Å}^2$. This was a B crystal. It has been possible to prepare single crystals belonging to the different varieties and to study the conditions of passage from one to the other.²⁶

Triglycerides

Triglycerides have two crystalline forms: one stable, where the chains are inclined, the other unstable with the molecules vertical to the stratification plane. The density being 1.03, one finds for all the homologues between C₁₀ and C₁₈, a molecular area of 64Å² for the stable and 56Å² for the unstable form.²⁷ The first value is about $3 \times 21\text{Å}^2$ (form B of the acids) while the second approaches 3×18.5 (cross section of the chains). It must be emphasized that long chain paraffins which have generally vertical molecules, give a

²⁴ More exactly: 53°, 63° and 71° for stearic acid.

²⁵ This calculation is based on the fact that the fatty acids have a monoclinic structure (the unit cell being a parallelepiped with a rectangular base) and the molecules fixed at each corner and at the center of the base are parallel to the tilted sides of the cell.

²⁶ Dupré La Tour, *Ann. de physique* [10] **18**, 199 (1932).

²⁷ The data for the spacing have been taken from Trillat and Nowarowski, *Ann. de physique* [10] **15**, 463 (1931) and Clarkson and Malkin, *J. Chem. Soc.* 666 (1934).

²³ See for example: Francis, Piper and Malkin, *Proc. Roy. Soc. A* **128**, 124 (1930).

calculated cross section of 18.5\AA^2 . This shows that the packing in the acids and triglycerides is governed mainly, if not completely, by the chains.

INTERPRETATION OF THE MOLECULAR AREAS FOUND IN THE SOLID MONOLAYERS

The simple comparison of the x-ray data with those obtained from solid films allows us to derive some conclusions as to the state of the molecules in the films. First, the 18.5\AA^2 area found at the breaking point of the acids, and the minimum area of $55\text{--}56\text{\AA}^2$ found at the collapsing point of the triglycerides, show that at these points the molecules are vertical. It is certainly not a simple coincidence that the 63\AA^2 found with the triglyceride solid layers as well as the 20.5 measured at the point of sublimation M of the acid (Fig. 5) agree with the x-ray data of both the stable form in triglycerides and the B form of acids.²⁸ Likewise, as will be seen with the mesomorphous films, in a certain well-defined range of temperature, acids give the molecular area of $23\text{--}24\text{\AA}^2$ which corresponds to the C form. These later films when compressed show a very distinct break at 19.5\AA^2 , showing the transition to the A form (Fig. 14). Triglycerides give also in a well-defined range of temperature a new form with a molecular area of 71\AA^2 (Fig. 13) which may be related to the C form of the acids ($71 = 3 \times 23.7$).

Since the molecular area is the same in the film and in the crystal, and undergoes a parallel modification, we are led to believe that *the lattice structure and the tilt of the molecules in the different forms are the same both in two and three dimensions*. It should be emphasized that once we admit this identity of structure, the only way we can interpret the variation of the area in the film on compression is by a progressive change of the tilt. We can no longer make use of the assumption

²⁸ Lyons and Rideal (Proc. Roy. Soc. **A99**, 33 (1921)) have attempted to explain the value 20.5\AA^2 , as well as that occasionally observed at about 26\AA^2 , on the supposition that they correspond, respectively, to two inclinations which permit different modes of interlocking of the zigzag chains. This hypothesis does not, however, explain the other characteristic values (19.5 and 23.5\AA^2). In any case, we are not concerned here with explaining the different modes of crystallization, but merely with showing the correspondence of the several forms in two and three dimensions.

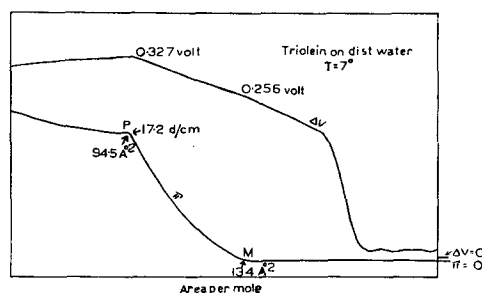


FIG. 6. Registered curves of a liquid film: triolein on distilled water at 7° .

that the molecules are always vertical and that the changes in area are due to changes in packing with "closed packed chains" or "closed packed heads" (Adam). As we have shown, the changes are due entirely to the tilt of the *chains* in the lattice, the cross section of the molecule remaining the same in acids and paraffins.

Liquid films

Let us consider the case of monolayers formed from substances which are liquid in three dimensions at the experimental temperature: for example oleic acid or triolein. Fig. 6 (triolein) shows a typical isotherm given by such films. At all pressures the film appears to be fluid and surface viscosity measurements reveal no anomalies or rigidity. The mean compressibility is 10 to 15 times greater than that of a solid film. In this case, as will be shown, the point M corresponds to the end of the condensation of the vapor phase into a two-dimensional liquid.²⁹ The point P indicates the limit of compression of the liquid monolayer: as the substance is liquid in three dimensions, the molecules which leave the surface collect into droplets or spots.

Some *solid substances*, such as stearic acid and trimyristin, form *solid films* at room temperature. But, provided the temperature is greater than a critical temperature of crystallization T_{cc} (different for different substances), it is possible to form, from solid substances, fluid films with isotherms similar to those of oleic acid and triolein (Fig. 1, V). Table I presents, for a series of substances, this minimum temperature T_{cc} and the areas at M and P .

²⁹ On the graph, the horizontal part corresponding to condensation is indistinguishable from the axis.

TABLE I.

	T_{cc}	AREA AT P	AREA AT M	$V^{2/3}/(\text{CALC.})$
Lauric Acid C_{12}	$<0^\circ$	$26A^2$	—	—
Myristic Acid C_{14}	34°	$27-28A^2$	$57-58A^2$	$57A^2$
Palmitic Acid C_{16}	55°	27	61	62
Oleic Acid C_{18}	$<0^\circ$	$26.5(4^\circ), 29(20^\circ)$	56	64
Elaidic Acid C_{18}	.	.	.	64
Tariric Acid C_{18}	.	$28-30$.	64
Trilaurin C_{12}	21°	$78-80$	$110-115$	111
Trimyristin C_{14}	43°	$85-86$	$120-124$	121
Triolein C_{18}	$<0^\circ$	$95-97$	$132-137(20^\circ)$	138
Taririn C_{18}	$<0^\circ$	$84(6^\circ)88(20^\circ)$	$132-134$	130
Glycol dilaurate*	$<0^\circ$	55	83	86 ($\partial=0.87$) 69 ($\partial=1.16$ at 80°)
Tribenzoin	$<0^\circ$	60	$75(3^\circ)$	

* From Adam, Proc. Roy. Soc. A126, 366 (1930)

Structure of the liquid film at the point P

One notices that the areas per chain at the point P do not vary much with the chain length³⁰ indicating the molecules are standing on the surface; but the area of 27 to $30A^2$ per chain proves that they are not vertical and close packed.

Proceeding from Langmuir's fundamental notion that the polar and nonpolar ends of the long chain molecules act independently, we shall describe the structure of liquid films at the points P and M , without making the further assumptions which he introduced in his theory of duplex films.³¹ Whereas in that paper, Langmuir was principally interested in obtaining an equation of state, we are here concerned with finding the structural correspondence between the two- and three-dimensional liquid states.

Let γ_b be the surface tension of the liquid which is spread and γ_{ab} its interfacial tension with water. If we represent by γ' the surface tension of water covered with a film at the point P , we find *experimentally*³² that:

$$\gamma' = \gamma_b + \gamma_{ab}. \quad (8)$$

As γ' represents the surface free energy, we may regard it as the sum of two different surface free energies ($\gamma_b' + \gamma_{ab}'$) localized at the upper and lower face, respectively, of the monolayer.

³⁰ Tribenzoin which gives a definitely different area is not a long chain compound.

³¹ I. Langmuir, reference 9.

³² This is another way of stating that at the point P , the surface pressure π is equal to the spreading coefficient $\pi = \gamma_a - (\gamma_b + \gamma_{ab})$ for $\pi = \gamma_a - \gamma'$ (where γ_a is the surface tension of pure water). This is an important deduction, since (8) indicates that the contact angles of the first droplets are zero when the equilibrium is stated in terms of Neumann's triangle, $\gamma' = \gamma_b \cos a + \gamma_{ab} \cos b$.

It follows then from (8) that

$$\gamma_b' + \gamma_{ab}' = \gamma_b + \gamma_{ab}.$$

We now assume that this equality is a consequence of the identity of the two members, that is $\gamma_b' = \gamma_b$ and $\gamma_{ab}' = \gamma_{ab}$.

From this it follows that, on one hand at the water interface of the film as well as under a thick oil layer, the polar groups occupy the same space and relative positions and, on the other hand, at the air interface, the orientation and packing of the chains are the same in the film and at the surface of a three-dimensional liquid.

This basic assumption ($\gamma_b' = \gamma_b$ and $\gamma_{ab}' = \gamma_{ab}$) is justified by a series of facts. First of all, experiments of the difference in wettability between the two faces of a slab of fatty acid solidified at the surface of water (A. Pockels, H. Devaux), lead to the view that the molecules of the lower part of the oil thick layer have their COOH groups turned to the water, while those at the surface turn their paraffin chains towards the air.

Using the ordinary method, we have measured the change of the water-air interface potential affected, not by a monolayer, but by a layer of several millimeters of oil. Practically the same value as that at the point P was found. As the potential lowering depends on the surface concentration, we may deduce that the number of COOH groups in contact with the water is the same in both cases.

As to the air-oil surface, it is generally accepted that liquids show a surface orientation. For fatty substances more particularly, both x-ray spectroscopy (method of the tangent drop),³³ and the elliptical polarization of the reflected light³⁴ give us conclusive evidence. Consideration of the correction of Eötvös constant leads us to infer that the molecules at the surface of liquid alcohols and acids occupy an area of about $25A^2$.³⁵

We thus assume that in its structure and concentration, the liquid monolayer at the point P is a reproduction of the surface of the three-dimensional liquid.

³³ Trillat and Nowarowski, Ann. de physique [10] 1, 467 (1931).

³⁴ Ch. Bouhet, Ann. de physique [10] 15, 5 (1931).

³⁵ E. K. Rideal, Surface Chemistry (1930), p. 38, and D. G. Dervichian, Comptes rendus 200, 2065 (1935).

Definition of an isotropic monolayer

At the surface of a liquid, the area occupied by a molecule is relatively small in comparison to the height: the space occupied by each molecule being a long prism or cylinder. In the bulk of the isotropic liquid, however, all directions are equivalent and thus the mean space per molecule is a cube whose volume is the molecular volume $V = M/N\bar{v}$. We can imagine an isotropic monolayer in which all the possible *directions* of the molecules would be equally distributed at random. For such an isotropic layer, the *mean thickness* and the *mean base area* per molecule would be the height and the base of the cube V (i.e., $V^{1/3}$ and $V^{2/3}$). For example, the thickness of an isotropic liquid film of palmitic acid would be 7.9Å instead of the 17.8 found at the point P , and the molecular area 62Å² instead of the 27Å². Thus the degree of anisotropy of liquid films can be defined by comparing the areas measured at different points of the isotherms to the area $A = V^{2/3}$ corresponding to the molecular volume of the isotropic liquid.

Structure of the liquid film at the point M

The last column of Table I gives the calculated values of $V^{1/3}$. It can be seen how close these values are to those found for the area at the point M .³⁶ We can at least conclude that at any rate the packing of the molecules in this type of film is not looser than in the three-dimensional liquid and the name of "expanded liquid" given to them is not justified. We shall adopt the simple terminology of "liquid film" and say that, *at the point of vaporization M , the state of the molecules is similar to what it is in the bulk of the three-dimensional isotropic liquid.*

Interpretation.—We can express the pressure π_P at the point P in terms of the work of cohesion ($W_b = 2\gamma_b$) of the spreading liquid and of its

work of adhesion ($W_{ab} = \gamma_a + \gamma_b - \gamma_{ab}$) to the water. From the definition of the surface pressure ($\pi_P = \gamma_a - \gamma'^{32}$) and from (8), we find:

$$\pi_P = W_{ab} - W_b. \quad (9)$$

This expression has an immediate physical significance. It shows that if the affinity of the fatty substance for water is greater than the cohesion between its own molecules, these will leave the deposited drop with a pressure which depends on the difference between the two free energies.

Let us again consider the film at P as a very flat drop, one molecule thick, to which may still be applied the notion of a work of cohesion and a work of adhesion. These free energies always refer to an area of 1 sq. cm. Then, if starting from P , we go down the isotherm by expanding the film, the free energy of cohesion and the free energy of adhesion will gradually decrease, not only on account of the decrease of molecular concentration per sq. cm, but also as a consequence of the variation of the intermolecular actions which are also related to the concentration. W_{ab} and W_b being particular values at the point P , let w_{ab} and w_b be the variable quantities corresponding at each given surface concentration. Whatever is the variation law of these two functions, we can write for every surface concentration:

$$\pi = w_{ab} - w_b \quad (10)$$

and note that this difference decreases with increasing the area per molecule. At the point M , π is practically negligible³⁷ and $w_{ab} = w_b$. This means that, at the point M , actions due to cohesion and those due to adhesion counterbalance one another, although both are still important. As the molecules are submitted on the average to isotropic actions, the state of the film will reproduce the state of a liquid in the bulk.

If $l_0 = V^{1/3}$ represents the mean intermolecular distance in the three-dimensional isotropic liquid, the relation $A_m = V^{2/3}$, which relates the area at M to the molecular volume, can also be written $A_M = l_0^2$. This expresses the fact that l_0 is a critical intermolecular distance which occurs both in fluids in bulk and in monolayers.

³⁷ The pressure at the transition is generally less than 0.2 dyne/cm, while it has 20 or 30 dynes at P .

³⁶ The early investigators used to measure the area at the point M (maximum extension). They considered the molecules isotropic in shape and taking M for the point where they come into contact, they tried to compare the thickness of the film with the calculated value $V^{1/3}$ (which comes to $A = V^{2/3}$). Very satisfactory agreement was thus found (Lord Rayleigh, Devaux, Labrouste). It is curious to notice how, when Langmuir established that the molecules in question were elongated, these results were forgotten or considered as a meaningless coincidence. Langmuir's determinations were concerned more especially with solid or mesomorphous films whilst these dealt with liquid films.

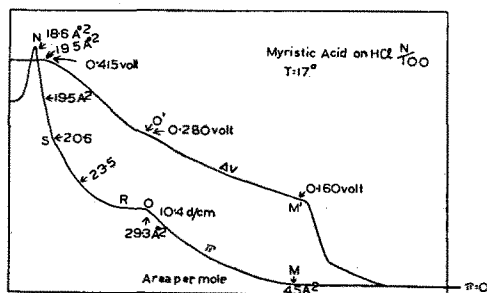


FIG. 7. Registered curves of a liquid film solidifying under compression: Myristic acid on HCl $N/100$ at 17° . Between M and O the film is liquid. OR is the crystallization transition which leads to the expanded mesomorphous state. On further compression, the mesomorphous (23.5Å^2) and then the solid S (20.5 , 19.5) states are reached. The film breaks at 18.6Å^2 (cross section of the vertical molecule).

Isotherms without discontinuous vapor-liquid transition (Fig. 1 or 2, VI).—In some cases, the expansion may gradually decrease w_{ab} and w_b but their difference $w_{ab} - w_b$ may remain relatively important. Then the film will be transformed into the gaseous state in a continuous manner giving an isotherm similar to a fluid which is above its critical temperature. This happens: 1.—with molecules having a second attractive group for water, which increases w_{ab} ; 2.—with short chain molecules, which possess a relatively higher thermal agitation and consequently a smaller w_b .

Solidification of liquid films by compression ($T < T_{cc}$)

This case is illustrated by Fig. 7 which reproduces the registered isotherm of myristic acid at 17°C ($T_{cc} = 34^\circ$). This curve has a lower part similar to the isotherm of a liquid film and an upper part analogous to that of a solid film of stearic acid (Fig. 14); an intermediate more or less horizontal transition, followed by a rounded part, joins these two regions. The isotherm of trilaurine at 7.7° ($T_{cc} = 21^\circ$) shows also an intermediate transition (Fig. 9). Both films are fluid between M and O and show viscosities comparable to those of films spread from liquid substances like oleic acid or triolein. Between S and N , the films are solid. This is shown by the break at N with myristic acid and the values of the area and the ΔV at S and N (20.5 and 18.5 for the acid, 64 and 56 for the triglyceride) compared with Figs. 5 and 14.

The end of the liquid state is indicated by a marked discontinuity at O showing the beginning of the transformation. As will be proved, the rounded part RS corresponds to the mesomorphous state through which the film passes before reaching the solid state. The flat part OR will be termed "crystallization transition." Theoretically the isotherm from O to R should be flat. In fact, since the transformation takes place between a highly oriented liquid and a liquid crystal and is accompanied by a change in area of only a few Å^2 , one cannot expect to observe a marked transition (Figs. 7, 8 and 9). On the other hand, for some substances of the type illustrated by Fig. 2 (for examples see reference 14) the difference in area $O - R$ between the two phases is much larger and the corresponding portion of the experimental isotherm is very nearly horizontal. When the temperature is lowered, this transition occurs at lower pressures and, under a certain temperature T_i , the liquid state disappears. Conversely, above a well determined temperature T_{cc} , after the

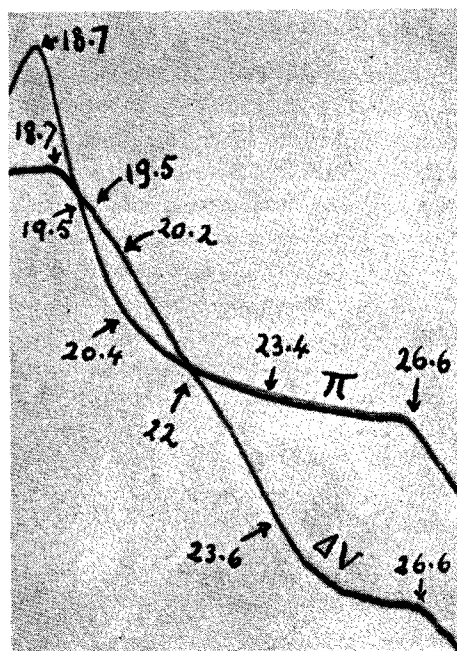
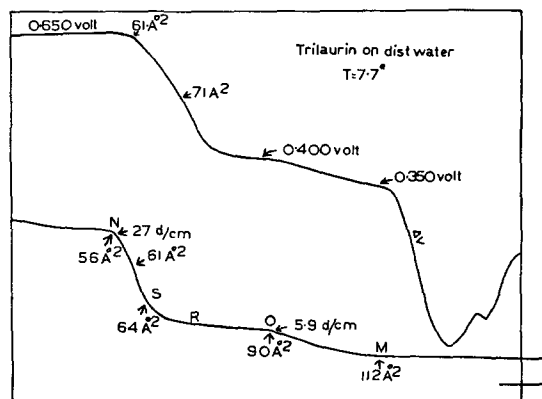


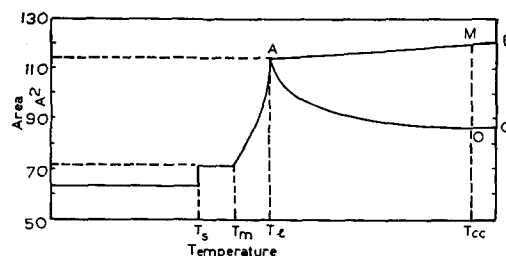
FIG. 8. Photographic reproduction at the actual size of part of a registered graph for myristic acid on HCl $N/100$. On the ΔV curve, the transition is particularly well marked. All the points of discontinuities of higher order are indicated. They correspond to changes of slope on both curves and are readily discerned. One of the curves is always slightly shifted with respect to the other. This is due to the recording system.

The classical series of isotherms obtained by Adam and Jessop with myristic acid are summarized by curves III, IV and V of Fig. 1.⁸⁸ It will be noticed, that with decreasing temperature, the domain of existence (*MO*) of the liquid



shortens. In Fig. 10 are plotted the corresponding areas of the M and O end points of the liquid state at different temperatures. The upper line AB represents the expansion of the liquid under its own vapor pressure. The lower part AC gives, for every temperature, the area at which the liquid is transformed into the mesomorphous phase. The temperature corresponding to the point A is that which we have previously denoted by T_l and termed the temperature of liquefaction under the saturated vapor pressure. From Figs. 1 and 2, one can see that this is a triple point, being the point of junction of three domains: the liquid, the vapor and the mesomorphous phases. The area at that point is 38–39 Å² for one chain molecules and 110–115 for triglycerides. It will be noticed that this later value is equal to three times 38–39.

³⁸ Similar isotherms have been obtained with trilaureine and trimyristine by D. G. Dervichian, *Ann. de physique*, reference 1.



higher order. This was already found in highly compressed gaseous films (see above), but exists also in films like oleic acid, triolein ($T > T_{cc}$) or myristic acid ($T_l < T < T_{cc}$). The same area per chain is found for both saturated and unsaturated chains, acids or triglycerides (triolein, tricaproin, tricaprylin). Figs. 11 and 12 show that, for this area, the compressibility, viscosity and apparent moment curves have a singularity, while the isotherm is quite smooth. Even for substances like triricinolein, in addition to the particular higher order point due to the presence

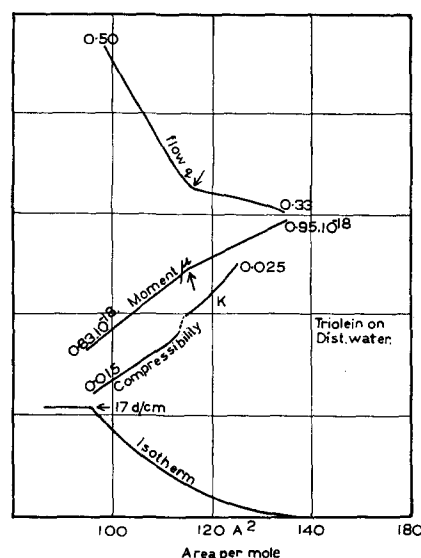


FIG. 11. Higher order transformation point in a liquid film ($T > T_{cl}$): Triolein on distilled water at room temperature. The fluidity, moment and compressibility curves show the existence of a second-order transformation at about 115\AA^2 (corresponding to the triple point area).

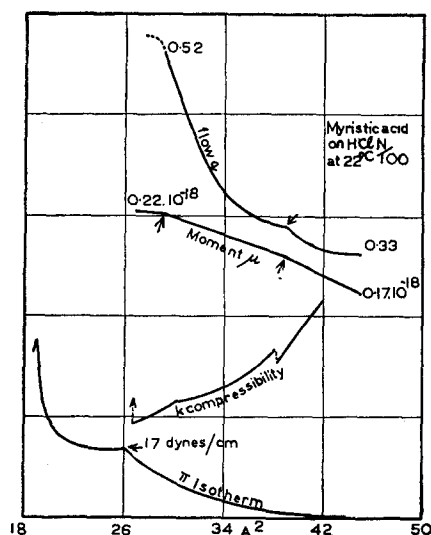


FIG. 12. Higher order transformation point in a liquid film ($T_{el} > T > T_l$): Myristic acid on HCl N/100 at 22°. Marked discontinuity at 38–39A² (corresponding to the triple point area), and apparently another towards 28–29 (corresponding to the point P).

of the supplementary alcoholic group, the 39A² point is found.

Liquid films of trilaurin and trimyristin, do not seem to present any higher order discontinuity; but it will be noticed that the maximum area of these substances as liquid films is 110–120A² (point of vaporization M), so that it may be confused with the point of higher discontinuity if it exists.

The mesomorphous state

When the temperature is gradually increased, solid films pass by a well-defined intermediate state before reaching the liquid state. We have previously called this the mesomorphous state. We shall try to identify it with a three-dimensional corresponding state.

1. *Transition from the solid to the mesomorphous state.*—At any temperature below 21°, the film of trimyristin is solid and gives at the point M the characteristic area of 63A². But at about 21° the area at M changes suddenly to 71A² and remains constant over another range of temperature. The isotherm then appears as in Fig. 13. The same state is found with the higher homologs of the triglycerides at higher temperatures. But the range of existence of this state is much more extended with acids on dilute HCl. Fig. 14 depicts stearic acid spread on HCl N/500. The

C₁₆, C₁₈, C₂₀ and C₂₂ acids give the same curve on dilute HCl. The area at the point M is 23.5A² which is the third of 71A². For the lower members of the series (myristic acid or trilaurine), the range of existence of this form is certainly below 0°. ³⁹ The film is fluid and stays so up to the point M' where it turns into solid.

2. *Labrouste's transformation.*—The expanded mesomorphous state.—The isotherms given by Adam and Jessop bring into prominence the

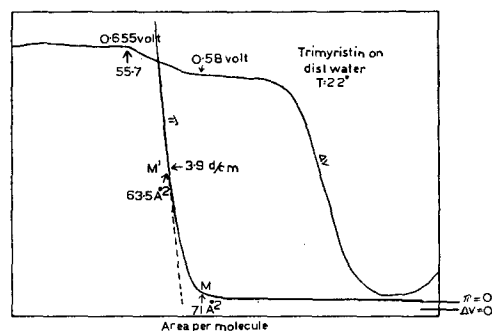


FIG. 13. Registered curves of a film showing the mesomorphous state ($T_m > T > T_s$): Trimyristin on distilled water at 22°. Compare with Fig. 5. The characteristic area of 63.5 appears here at M' as a transition of higher order.

evolution of the films after the liquid state has made its appearance. But before the real melting occurs and starting from the 23.5A² state, another transformation which has been more specially studied by Labrouste takes place. Labrouste's experiments were confined to variations of the area at the point M with the temperature. No measurements of pressure were made at that time and some important points could not be noted without a record of the complete isotherm. Fig. 10 has been plotted from results drawn from a great number of isotherms registered at different temperatures. They refer to trimyristin. As abscissa are indicated the temperatures and ordinates the corresponding areas at the vaporization point M (except the part AC). We note the discontinuous transition from the 63 to the 71 form at the temperature T_s (21°). This area remains constant up to a new point T_m (24°). Then a gradual expansion commences: the expansion coefficient goes on increasing and

³⁹ For the range of existence of this state, it must be noticed that besides the temperature, the nature of the substrate has to be considered, specially in the case of the acids (Adam and Miller Proc. Roy. Soc. A142, 401 and 416 (1933)).

finally attains a very high value when liquefaction is reached. Beginning from that point, the expansion at the point *M* proceeds more slowly following a slightly inclined straight line.

On the isotherms the lower part becomes more and more rounded and lengthens (Fig. 15); then suddenly at a temperature $T_l(29^\circ)$ the characteristic type of curve of the liquid state appears. Over this range of temperature the film is still fluid. Films which give isotherms similar to Fig. 15 will be said to be in the expanded mesomorphous state.

3. *Transition from the expanded mesomorphous to the liquid state.*—The transition from the expanded mesomorphous to the liquid phase by increase of temperature occurs under its own vapor pressure at the point T_l . Above this temperature, the transition may be obtained by compression along the different flats of the Adam and Jessop's isotherms (Figs. 7, 8 and 9). The assumption of Langmuir⁹ of the formation of "micelles" of a small number of molecules to explain these flats cannot be supported if we consider that, even with the relatively large dimensions of the electrode used, the inhomogeneity of the film in this region is detected on the registered potential curve. Corresponding to the kink point *O* of the isotherm, on this appears a flat horizontal part which varies from diagram

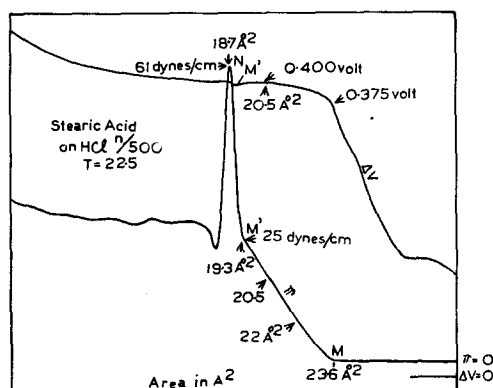


FIG. 14. Registered curves of a film showing the mesomorphous state ($T_m > T > T_s$): Stearic acid on HCl *N*/500 at 22.5° . The 22Å^2 point can be noticed on the isotherm by a slight change of slope. The 19.5 point is clearly marked; above it the film is in an unstable state. After the break at 18.7Å^2 , the pressure falls approximately to the value corresponding to the 19.3 point (the film is no longer homogeneous). Note the maximum value of the ΔV at 20.5Å^2 and the minimum corresponding to 19.3Å^2 . On many graphs the isotherm itself shows a slight kink at 20.5Å^2 .

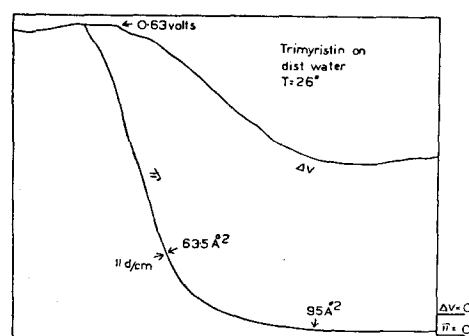


FIG. 15. Registered curves showing the expanded mesomorphous state ($T_l > T > T_m$): trimyristin on distilled water at 26° .

to diagram according to the fluctuations of relative concentrations of both phases under the electrode.⁴⁰ There is an ordinary transition probably from a state of disorder—or at least very similar to the liquid state—to a crystalline state. The crystalline state is the *expanded* mesomorphous, since this is the last form we meet before the liquid phase. The rounded part *RS* after the kink corresponds to the compression of the expanded mesomorphous phase and leads continuously to the solid. In other words, it is the reproduction at a higher pressure of the isotherm of Fig. 14.

Identification of the mesomorphous state

On the mesomorphous phase isotherms (Figs. 13, 14, 15), the transition from the *C* form (23.5) to the *A* form (19.5) is continuous from *M* to *M'*. There is only a discontinuity in the compressibility at *M'*. This is a transformation of the second order and shows that the change which occurs is from a given state of order to another state of order. We conclude, from this and from the fact that the area of 23.5Å^2 corresponds to a well-defined crystalline form, that the mesomorphous films have a crystalline structure and must correspond to three-dimensional liquid crystals. We note also that the expansion curve in Fig. 10 is similar to that found in studying, in three dimensions, the change of volume of substances such as para-azoxy-phenetol or para-azoxy-anisol in their

⁴⁰ This unquestionably confirms once more the existence of transition even on the electrical curve, as was first detected by Schulman and Rideal, reference 3, and questioned by N. K. Adam (Proc. Roy. Soc. A138, 411 (1932)).

known and corresponds to the stable form, the other, about twenty degrees lower, corresponds to an unstable form. Clarkson and Malkin who have carried out a systematic x-ray study of the triglycerides, call this second variety the *vitrous form*. The diagrams of this form do not show any large spacing periodicity. The stable form of tripalmitin, for example, melts at 65°. If the melt be suddenly cooled, a solid is obtained which, on increasing the temperature, melts at 45°, remains fluid for a while and then solidifies to melt again at the normal temperature of 65°. In Table II are listed the melting points in monolayers with those of the ordinary and vitrous forms in three dimensions (where known).

As far as the triglycerides are concerned, we note that T_i is practically the same as the melting point of the vitrous form in three dimensions. Labrouste has clearly established that the substance spread in monolayer form is the vitrous variety. The triglyceride was spread, then compressed till particles visible under the microscope were obtained and placed on a slide. By raising the temperature, these particles melted at the melting point of the vitrous form and after a while gave the stable form. Moreover, the vitrous solid form spreads spontaneously on the water up to very high pressures, while the crystal spreads with greater difficulty.

It may be concluded, that *the vitrous form of the triglycerides, while unstable under ordinary conditions, is the stable state in surface layers*. For the acids and alcohols, we may say that the

TABLE III. Different characteristic areas.

CHARACTERISTIC AREAS	SOLID FILMS	MESO-MORPHOUS FILMS	EX-PANDED MESO-MORPHOUS	LIQUID FILMS	GASEOUS FILMS
18.5 (cross section)	18.5	18.5	18.5		
19.5 (form A)	19.5	19.5	19.5		
20.5 (form B)	20.5	20.5	20.5		
22 (?)		22	22		
23.5 (form C)		23.5	23.5		
27-30 (surf. of liq.)			24.5 to 26.5	27-30	27-30
38-39 (triple point) $V^{\frac{1}{3}}$ (isotropic layer)				38-39 $V^{\frac{1}{3}}$	38-39

vitrous form which is unknown in three dimensions, can exist only in monolayers.

SIGNIFICANCE OF THE CRITICAL TEMPERATURE OF CRYSTALLIZATION T_{cc}

Labrouste carried out a series of experiments on the vitrous form of the triglycerides which have a direct bearing on the behavior of monolayers. We have noted that when melting at the lower temperature, the vitrous form persisted for a while before solidifying again. This period in the metastable state increases with the temperature at which the fused vitrous form is kept (e.g. for trimyristin: 10 seconds at 34°, 100 sec. at 43°). Fig. 17 gives a curve redrawn from the data of Labrouste for trimyristin. Times have been plotted against the temperature. As was noticed by Labrouste, 30-31° is the melting point of the vitrous form and the temperature at which it is spontaneously transformed to the stable form without melting. But we also note that the curve is asymptotic towards 44-45°, indicating that over this temperature the substance can remain indefinitely melted. It is interesting to note that this temperature coincides with the critical temperature of solidification T_{cc} in the films of trimyristin. When Labrouste carried out his experiments, the critical phenomena in monolayers were not yet known.

It is to be noticed that retarded solidification is also found in surface films⁴³ and thus qualita-

⁴³ D. G. Dervichian, Ann. de physique [11] 8, (1937).

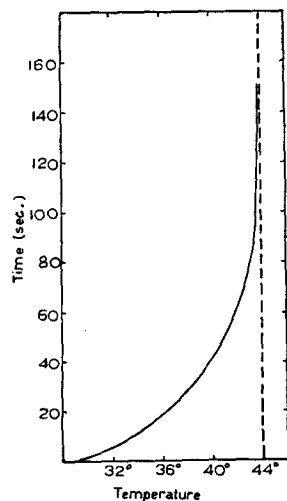


FIG. 17. Period of persistence of the melted vitrous form of trimyristin as a function of the temperature (redrawn from the data of Labrouste).

tively corroborates Labrouste's results in three dimensions.

List of possible singular areas

It has been noticed that *some of the characteristic areas corresponding to higher order transitions in phases which exist at higher temperatures are precisely those which correspond to ordinary phase transition of the first order at lower temperatures.*

The Table III summarizes this general relation. Areas corresponding to discontinuities of the first order (ordinary change of phase) are printed in heavy type. Those referring to higher order discontinuities are printed in ordinary type.

CONCLUSIONS

(1) From the fact that different substances give different types of isotherms conclusions are frequently drawn on the influence of molecular constitution on the force area characteristics. This is likely to lead to erroneous results unless care is taken to compare the monolayers in corresponding physical states.

(2) We are naturally led to inquire whether there exist, *in three dimensions*, relations analogous to those illustrated by Table III. That such relations do in fact exist is confirmed by the data of Schroer⁴³ on the compressibility of ether over a wide range of temperature including the critical temperature. Discontinuities of higher order appear at temperatures well above the critical, when the volume reaches values near the critical volume. Furthermore x-ray analysis indicates traces of organization in the same region.⁴⁴

Published data on the compressibility of three-dimensional liquids are unfortunately not sufficient to show up corresponding discontinuities in the neighborhood of the triple point volume.

I wish to express my sincere thanks to Professor E. K. Rideal for much help and criticism during the writing of this paper.

⁴³ Schroer, *Zeits. f. physik. Chemie* **140**, 381 (1929).

⁴⁴ Cybotactic condition. See W. Noll, *Phys. Rev.* **42**, 336 (1932); R. D. Spangler, *Phys. Rev.* **46**, 698 (1934); Benz and Stewart, *Phys. Rev.* **46**, 703 (1934).

Partition Functions for Partly Classical Systems

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A method is described for calculating the partition function of systems whose Hamiltonian operator separates into three terms of the following types. The first and second terms are functions of different sets of coordinates while the third is a small coupling term. The energy levels of the first term by itself are widely spaced compared to kT while those of the second are closely spaced. In the result given, the partition function becomes a sum over the widely spaced levels and a phase integral for the contribution of the other levels, as in the case with no coupling term, but here the effect of the coupling term is included in the integral. As an illustration it is shown that the coupling of rotational and vibrational angular momentum in a polyatomic molecule has no appreciable effect on the thermodynamic properties even though it has a marked effect on the energy levels.

IN many systems it is possible to separate the Hamiltonian operator into two terms, each involving different coordinates, such that one term leads to closely spaced and the other to widely spaced energy levels. The partition function for a separable system can be written as a product of two factors and in this case the factor involving closely spaced energy levels can often

be accurately approximated by an integral related to the classical phase integral.

In other cases, however, the Hamiltonian contains a third term, small but not negligible, which is a function of both sets of coordinates so that a strict separation cannot be carried out. It is the purpose of this note to show how such cases may be handled, retaining the phase integral ap-