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Transformation Diagrams for the Collapse of a Phospholipid Monolayer

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Abstract

The kinetics of phase transitions in three-dimensional bulk materials are commonly presented in transformation diagrams. Time–temperature transformation (TTT) and continuous-cooling-transformation (CCT) diagrams plot the time required to transform specific fractions of the material to the new phase by cooling below a transition temperature. Transformation occurs isothermally for the TTT diagrams and during continuous cooling through a range of temperatures for CCT curves. Here we present analogous transformation diagrams for two-dimensional monolayers, which collapse at the equilibrium spreading pressure (π_e) to form a three-dimensional bulk phase. Time–surface pressure–transformation ($T\pi T$) diagrams give the time required for specific fractions of the film to collapse when surface pressure is constant, and continuous-compression-transformation diagrams give the same information when surface pressure varies continuously. The diagrams, constructed here from previously reported data for 1-palmitoyl-2-oleoyl phosphatidylcholine, provide insights into the behavior of the films. The $T\pi T$ diagrams successfully predict the existence and approximate magnitude of a threshold rate for compressing the films to high surface pressures above π_e and the approximate shape of isotherms obtained with different rates of interfacial compression. The diagrams also caution that the behavior of mixed monolayers, explained previously in terms of compositional changes, can instead result from collapse that varies with surface pressure. Finally, the similarity between the shapes of the TTT and $T\pi T$ diagrams, with the time for transformation passing through a minimum and then increasing as the systems deviate further from equilibrium, suggests that analogous mechanisms determine the behavior of both systems.

1. Introduction

Monomolecular films at an air/water interface undergo well-known phase transitions. In addition to transformations between two-dimensional phases, the interfacial monolayers can also collapse, forming a three-dimensional bulk phase that coexists with the monolayer at the equilibrium spreading pressure (π_e).¹ At surface pressures (π) above π_e , the two phases are no longer in equilibrium and collapse progresses. Formation of a bulk phase from the monolayer at constant π produces a decrease in interfacial area, which can be used to characterize the kinetics of collapse. Previous studies have focused on rates of area-decay at a single, constant π ^{2–4} and on the effects of increasing π .^{2,5–8} Although, according to those studies, rates of collapse should increase with greater $\Delta\pi = \pi - \pi_e$, phosphatidylcholine (PC) films show an unexpected variation, observed first with measurements in a Langmuir trough⁹ and more recently on a captive bubble.^{10,11} For at least some PC monolayers in the fluid liquid-expanded (LE) phase, rates of collapse first increase with greater $\Delta\pi$ but then

slow (Figure 1). This paper focuses on the implications of the variable collapse for the behavior of films compressed at different rates.

The unexpected variation of collapse with $\Delta\pi$ is analogous to variations in rates of transformation found for some bulk materials during cooling below a transition temperature (T_c). For those materials, the kinetics of transformation are frequently described by time–temperature–transformation (TTT) diagrams,^{12,13} which show the time required at different temperatures for a fixed fraction (ξ) of the system to transform isothermally to the new phase (Figure 2a). TTT curves generally exhibit a C shape, characterized by a temperature at which the time needed for the material to transform reaches a minimum, commonly referred to as the “nose” of the diagram. To construct TTT curves from experimental data, temperatures below T_c are reached after a rapid quench, during which transformation is undetectable. The temperature is then held constant and the evolution of ξ with time (t) measured. Although TTT curves only describe the kinetics of the phase transition under isothermal conditions, they also provide a qualitative description of how the transformation will evolve during gradual cooling through a range of temperatures. For instance, the time required at the nose of the TTT to transform the smallest detectable amount of new phase determines the minimum rate of cooling necessary to avoid the phase transition when reaching temperatures below the nose. Because the extent of transformation depends nonlinearly on the cooling history as well as temperature, continuously cooled systems deviate to some degree from the predictions of the TTT diagrams. Continuous-cooling–transformation (CCT) diagrams,¹² which plot the temperature reached and the time required to attain a given extent of transformation, provide the exact behavior of the material when the temperature falls at continuous rates (Figure 3a). TTT diagrams nevertheless provide an important basis for understanding and approximately predicting the behavior of systems cooled along a variety of pathways.

Here we construct analogous transformation diagrams for the collapse of an interfacial monolayer. When the transformation occurs at constant π above π_c , the variation of interfacial area provides the kinetics of isobaric transformation and the basis for constructing time–surface pressure–transformation ($T\pi T$) diagrams (Figure 2b). Specific π are reached after an initial rapid compression, during which collapse is negligible. When the films are instead subjected to continuous rates of compression so that π increases above π_c gradually, the behavior of the systems can be plotted in continuous-compression–transformation (CCpT) diagrams (Figure 3b). Using previously published data obtained with 1-palmitoyl-2-oleoyl phosphatidylcholine (POPC),¹¹ we show the extent to which $T\pi T$ diagrams predict the general shape of CCpT diagrams and of isotherms obtained during compression along different pathways.

2. Experimental Procedure

Experimental data used in this paper to construct $T\pi T$ and CCpT diagrams have been published previously.¹¹ A brief summary of the experimental procedures used to obtain the data is presented here for completeness.

Measurements were performed on monomolecular films of POPC spread at the interface of an air bubble immersed in an aqueous medium. The captive bubble, used as a surface balance, has several important advantages over Langmuir troughs for these studies. The bubble provides a continuous closed interface that confines the film without barriers. The absence of barriers eliminates a potential site at which collapse might nucleate, as well as a site for the leakage that inevitably occurs at high π in troughs.⁹ The bubble can also attain faster rates of interfacial compression which allow the films to reach high π that are

frequently difficult to achieve using Langmuir troughs. A captive bubble therefore allows a more in-depth study of the effects of π on rates of collapse.

After spreading POPC at the air/water interface, and prior to any measurements, the spreading solvent was removed by exhaustive exchange of the subphase.¹⁴ The films were then compressed slowly, changing interfacial area (A) at an approximate rate of 0.005 min^{-1} , measured as $(1/A)(dA/dt)$, to an equilibrium state just below 46 mN m^{-1} . Experiments were performed at the constant temperature of 26°C , where π_e is approximately 46.9 mN m^{-1} .¹¹ The profile of the bubble along the horizontal axis was recorded with a CCD camera, captured to a computer, and used to calculate π , interfacial area, and volume.^{14–16}

Infusion of aqueous solution by a pump-controlled syringe into the chamber in which the bubble was submerged determined the rates of interfacial compression, which varied with time. During compressions at the highest rates, referred to simply as “fast compressions”, π could be increased from 46 to 68 mN m^{-1} in approximately 0.4 s , which corresponded to an initial change in area of approximately 24 min^{-1} . For the construction of $T\pi T$ diagrams, π was increased with an initial fast compression to target values, which were subsequently kept constant by means of simple feedback control.¹¹ Overshoot of target π by as much as 2 mN m^{-1} could occur immediately after the fast compression. Subsequent inaccuracies in the control of π were approximately 0.5 mN m^{-1} . Various constant rates of infusion, which produced constant rates of volumetric change between 0.05 and 72 min^{-1} when measured as $(1/V_0)(dV/dt)$, where V and V_0 are the bubble's current and initial volumes, respectively, were employed to obtain data for the $CC\pi T$ curves.

3. Results

3.1. $T\pi T$ Diagrams

For the collapsing monolayers, construction of $T\pi T$ diagrams required a means of following the extent of collapse. The rate at which the interfacial area shrinks because of collapse is approximately equal to the molecular area, or area per molecule, in the monolayer times the rate of molecular transfer to the collapsed phase. Area therefore provided an experimentally accessible indicator of transformation. The effect of viscoelasticity within the interface, however, could also contribute to changes in area. Under equilibrium conditions below π_e , the relationship between area and π is determined exclusively by the film's compressibility. When the film deviates from equilibrium, viscoelastic relaxation also contributes to changes in area.¹⁷ To follow collapse, our studies required a distinction between the effects on area-decay of collapse and viscoelasticity.

Our results provided a range of π over which viscoelastic relaxation after the fast compressions could be ignored. Measurements just above π_e required only a small deviation from equilibrium conditions at 46 mN m^{-1} , and therefore, relaxation should be negligible. Relaxation becomes more important when faster compressions and larger increases in π produce greater deviations from equilibrium. The amount of relaxation expected at high π was therefore estimated from fast compressions below π_e . Following a fast compression from 5 mN m^{-1} to π just below π_e , the surface area fell over the course of 15 min by 2.1% .¹¹ This value was considered an upper limit for the effect of relaxation at higher π . During measurements close to the nose of the $T\pi T$ diagram at approximately 50 mN m^{-1} , where rates of collapse are greatest, the area decreased in 15 min by more than 50% (Figure 1). Relaxation was therefore assumed to be negligible relative to collapse near the nose. Above approximately 62 mN m^{-1} , however, the area at constant π decreased in 15 min by less than 10% (Figure 1). At those higher π , relaxation might contribute a significant fraction of the change in area. Consequently, the analysis presented here was restricted to π

between π_e and 62 mN m^{-1} . In that range, we assumed that changes in the film's area at constant π provided an accurate measurement of collapse.

$T\pi T$ diagrams should reflect only the collapse that occurs at a specific π . Compressions from the initial equilibrium condition to the target π , therefore, should avoid collapse. Our results indicated that, during the rapid rise in π , the change in area resulting from collapse was small. Progressively faster compressions achieved high π with smaller changes in interfacial area, suggesting that less collapse occurred. With faster rates, the surface pressure–area (π – A) isotherms reached a limiting isotherm that had the same slope above π_e as equilibrium isotherms just below π_e , where collapse cannot occur.¹⁰ We therefore assumed that, during the fast compressions, the change in area of the monolayer resulted only from its compressibility.

Construction of the $T\pi T$ plots then required measurements of the change in area (ΔA) relative to the initial value (A_0) when the films first reached the target π and the time (t) over which ΔA occurred (Figure 4a). Experimental uncertainties were greatest near the completion of the fast compression when π first became constant, and determination of A_0 from the data for an individual experiment was sometimes difficult. Curves from several experiments, which were generally quite similar, were instead fitted to a linear relationship ($r^2 = 0.9994$) between area and π that was used to obtain A_0 at the different π achieved in the individual experiments. In determining the times for transformation, the duration of the fast compression was negligible compared to the time needed to achieve any fractional change in area considered here. Therefore, time was measured relative to the beginning of the fast compression rather than the point at which the film first reached the target π (Figure 4a).

The $T\pi T$ curves had the characteristic C shape of the TTT curves for bulk materials (Figure 5). The presence of a nose indicated the existence of a π at which collapse reached a maximum rate. The diagrams, however, did not convey that highest rate. Because collapse at each constant π slowed progressively (Figure 1), the initial rates immediately after reaching the target π were fastest. Although for bulk materials, TTT diagrams commonly include curves that capture the very beginning and end of the transformation, those levels were difficult to measure for the collapsing monolayers. Practical limitations prevented compression of the films to complete collapse, and experimental uncertainties prevented access to the very earliest stages. Consequently, the earliest, fastest stages of collapse were not represented in the $T\pi T$ diagrams. The rate at the nose of 0.3 min^{-1} , expressed as $d[\ln(A/A_0)]/dt$, which is equivalent to $(1/A)(dA/dt)$, and estimated as $\ln(0.95)$ divided by the average time required to reduce area by 5%, therefore represented a slight underestimate of the maximum rate.

3.2. CCpT Diagrams

CCpT diagrams were constructed from data obtained previously¹¹ by reducing the bubble's volume at different constant rates (Figure 6), which resulted in continuous compressions of interfacial area at different rates and different variations in π . Changes in rate over an order of magnitude produced π – A isotherms with a flat plateau at π that changed relatively little. At a threshold rate of compressing interfacial area, which was approximately 0.24 min^{-1} when measured during the first 5 s of compression, π abruptly increased. At and above that rate, π reached high values $> 65 \text{ mN m}^{-1}$. Close to the threshold, the π – A isotherms showed an initial steep rise in π followed by a segment with a much flatter slope before a final steep segment to high π . Increasing the rate of area-compression above the threshold produced progressively more linear increases in π with area.

Construction of the CCpT diagram again required determination of the change in area resulting from collapse and the associated times of transformation. Rates of compression were much slower than during the fast compressions used to reach the target π for the T π T diagrams, after which relaxation was assumed to be negligible. The effects of relaxation, which should be smaller during these slower compressions, were ignored. Changes in area were attributed to the combined effects of compressibility and collapse. π - A curves above π_c obtained during fast compressions, where collapse and relaxation were assumed to be negligible, indicated the film's compressibility. The decrease in area due to collapse at each π was therefore taken as the difference between the area reached during the fast compressions, calculated from the fitted linear relationship between area and π used in the construction of T π T plots, and the actual area obtained during the slower continuous compressions (Figure 4b). Time was measured relative to the beginning of the compression. CCpT curves then depict the collapse of the films along different compression pathways.

For π below the nose, the shapes of the CCpT and T π T plots (Figure 7) were essentially identical. The shift during this initial segment of the CCpT to longer times and lower π , expected by analogy with the diagrams for bulk materials, was not evident (Figure 7b). Above 50 mN m⁻¹, however, the CCpT curves deviated from the T π T curves to shorter times (Figure 7b). This divergence of the two transformation diagrams above the nose did correspond to the behavior of the bulk materials. The slower compressions used for construction of CCpT curves resulted in significant collapse at π near the nose, which the faster initial compressions used for the T π T avoided. Therefore the time to reach any given fractional decrease in area at π above the nose, where rates of collapse decrease, was significantly shorter for CCpT curves.

4. Discussion

4.1. Threshold Rate of Compression

The T π T diagram accurately predicts a number of behaviors observed during compression of the films at different rates. The existence of the nose, for instance, implies that to reach high π , films must undergo compression above a threshold rate. During compression, π rises only if molecular area decreases, and hence, the relative rates of collapse and compression determine the behavior of the film. The time for any fractional transformation reaches a minimum at the nose of the T π T, and rates of collapse therefore are maximal. For compression slower than collapse at the nose, π will rise only to the point at which the rates of the two processes are equal. If compressed at a series of increasing rates, π will remain below the nose until compression exceeds the maximum rate of collapse. Once compression is faster than collapse at the nose, the film will abruptly gain access not just to π immediately above the nose, but because of the decreasing rates of collapse, to higher π as well. The maximum rate of collapse therefore determines the threshold rate of compression for reaching high π .

The prediction of the threshold rate of compression is qualitative rather than quantitative. Although to reach high π , compression must be faster than collapse at the nose of the T π T, the behavior of the films complicates estimation of the minimum rates required to reach high π . Collapse varies at constant π , becoming progressively slower with time (Figure 1). Because of the slowing collapse, a film for which rates of compression and collapse initially become equal below the nose may still reach high π . The slowing collapse also means that the fastest rates occur at the earliest times after reaching the target π . Experimental uncertainties, however, are greatest during that part of the experiments, with π often overshooting the target value. The highest rates of collapse at any π are, therefore, difficult to measure. Given these uncertainties, the agreement between the threshold rate of initial

compression ($\sim 0.24 \text{ min}^{-1}$) and the maximum rate of initial collapse ($\sim 0.3 \text{ min}^{-1}$) is quite good.

Similar threshold rates can be calculated for bulk materials from the TTT diagrams. Cooling will only reach low temperatures if the rate of heat extraction exceeds the rate of latent heat production at the nose. Cooling, however, is commonly reported in terms of the intensive variable, temperature, rather than the removal of heat that would be analogous to the decrease in area for the monolayers. Reports for bulk materials usually discuss the minimum rate at which temperature must change to avoid detectable levels of transformation,^{18,19} rather than an absolute threshold for reaching low temperatures regardless of the extent of transformation. For experiments at constant rates of heat extraction, bulk materials would display a threshold for reaching low temperatures analogous to the threshold rate of compression discussed here for the films.

4.2. Behaviors during Continuous Compression

The $T\pi$ T curves explain the similarity below the nose between the CCpT and $T\pi$ T diagrams. Analogy to the diagrams for bulk materials predicts that, relative to the $T\pi$ T curves, the CCpT data should be shifted to longer times. During continuous compressions below the nose, the rate of collapse varies, with the most rapid collapse occurring at the final, highest π . Any fractional transformation should therefore require more time during a continuous compression than during collapse that occurs exclusively at the final π . The extent to which the CCpT curves are shifted, however, depends on how rapidly rates of collapse change below the nose. For POPC, the relatively horizontal initial segments of the $T\pi$ T curves indicate that π should rise quickly to the point at which rates of compression and collapse are equal. Most of the transformation during the continuous compression below the nose therefore occurs at constant π , resulting in CCpT and $T\pi$ T diagrams that are almost indistinguishable.

The variation of collapse with π , depicted in $T\pi$ T diagrams, also explains the shape of π - A compression isotherms above π_c and the changes observed when applying different rates of compression. The slope of the curves is determined by the compressibility of the monolayer and by the relative rates of compression and collapse. During compression at speeds below the threshold, π rises to the point at which the rates of compression and collapse are equal and then remains constant during further compression. This behavior produces an extended plateau in the π - A isotherm, with the progressive slowing of collapse resulting in a slightly positive slope. Faster compressions produce plateaus at higher π , a phenomenon that has also been observed for other surfactants.⁸ If compression rates greatly exceed threshold values then the monolayers reach high π with minimal collapse, and the slope of the isotherm reflects only the film's compressibility. During compression at intermediate rates that are only slightly above the threshold, the relative rates of compression and collapse at different π vary considerably and the slope changes accordingly. Initially, as π increases above π_c , compression exceeds collapse by a large margin, and π rises steeply. Near the nose, however, collapse is substantial and the similar rates of compression and collapse produce a slope of the π - A curve that is relatively flat. Beyond the nose, collapse slows and π therefore rises again. These predictions agree with the actual curves obtained experimentally for different rates of compression (Figure 6).

These results with single-component films raise a point of caution concerning the interpretation of isotherms for multicomponent monolayers. Films with coexisting phases that collapse at different rates can produce π - A isotherms that resemble the curves for POPC.²⁰ During moderately slow compression, the isotherms show a relatively flat plateau just above π_c , corresponding to the collapse of the more fluid phase, which eventually terminates after the exclusion of that phase with a steeply rising π that reflects the

compressibility of the remaining condensed phase. The $T\pi T$ diagram presented here shows that similar isotherms can occur with single-component films. The shape of the isotherm alone, therefore, does not necessarily indicate a change of composition and could instead reflect simply collapse of all constituents that varies with π . A careful analysis is then needed to identify which mechanism produces a plateau in isotherms of mixed films.

4.3. Variation of Collapse Rates with π

The similar C shape of both TTT and $T\pi T$ curves suggests that similar mechanisms affect transformation rates of bulk materials and interfacial films. The shape of TTT curves that describe the transformation of many bulk materials during cooling has been successfully explained by theories concerning nucleation and growth of the new phase.¹³ As temperature decreases below T_c , rates of both nucleation and growth initially increase and transformation proceeds more rapidly. Lower temperatures, however, diminish molecular thermal motions. Since the transformations require an activation energy to proceed and thermal fluctuations provide that energy, at some point during the fall in temperature, at least growth of the new phase slows and transformation rates decrease.^{13,21} In particular, during cooling of a bulk liquid phase below the melting temperature, T_m , the decrease in thermal motions gives rise to an increase in the fluid viscosity. According to the free-volume model, viscosity is proportional to $\exp[1/(v - v_0)]$, where v and v_0 are the specific volumes of the liquid and crystal phases, respectively.²² As temperature falls, $v - v_0$ decreases, producing an experimentally observed increase in viscosity. Eventually, viscosity becomes so large that rates of transformation to the crystal phase decrease. If temperature falls fast enough to sufficiently low levels, the fluid avoids crystallization and undergoes a glass transition.

An increase in the monolayer's lateral viscosity could also explain the C-shaped $T\pi T$ curves for the collapse of POPC and other fluid PC monolayers in the LE phase.¹⁰ Since π increases with surface concentration, the molecular area of a monolayer above π_c must be smaller than equilibrium values. The free-area model, which is analogous to the free volume of bulk materials, establishes that, at constant temperature, the film's diffusion coefficient is proportional to $\exp[-1/(a - a_0)]$, where a and a_0 are the actual and minimum molecular areas.^{23–26} Measurements of the diffusion coefficient confirm that compression decreases molecular motions.^{25,26} As a consequence of the restricted free area, viscosity, which is approximately proportional to the inverse of the diffusion coefficient in fluid systems,²⁷ should increase abruptly when a approaches a_0 and, particularly for the PC films considered here, collapse should slow. Several monolayers containing compounds that in the bulk phase form smectic liquid crystals collapse by flow of the monomolecular film into a stacked structure.^{28–32} The PCs apparently collapse by this mechanism.³³ An increase in viscosity should therefore cause at least rates of growth to slow.^{11,34,35} Experimental observations support this possibility. Regardless of the pathway along which the films are compressed, collapse slows at high π . Because the different pathways should produce differences in the number and size of collapsed nuclei,^{2,4,5} the similar rates of collapse imply that at least growth must decrease at π above the nose. An increase in viscosity, similar to the one that leads to a glass transition in supercooled bulk liquids, could therefore also result from compression of the monolayer. Supercompressed fluid monolayers would then join supercooled bulk liquids in the general category of jammed systems in which a wide variety of materials achieve rigidity characteristic of solids in response to changes in pressure, concentration, or temperature without fundamental changes in structure.^{36–38}

Despite a century of studies on insoluble monolayers, the analogous metastability of the fluid films at high surface pressures and bulk liquids at low temperatures has not been reported previously. Our use of a bubble as a surface balance may be important. The bubble allows much faster rates of compression, which may be necessary to reach high surface pressures above the nose and eliminates barriers that could provide sites for heterogeneous

nucleation of collapse. The slowing of collapse at high surface pressures, however, has been observed previously with phospholipid monolayers in studies on the Langmuir trough.⁹ Differences among the substances studied therefore may also be crucial. Prior studies, for instance, concerning collapse for fluid monolayers have largely used materials in which the bulk phase grows by addition of compounds all along its interface with the monolayer.^{6,39} For the liquid-crystalline collapse that apparently occurs for the LE phosphatidylcholines,³³ constituents instead flow to the new phase as an intact lamella through a constrained locus.^{29,30,32,33} Substances that collapse by different mechanisms might then become metastable at different surface pressures, some of which might be inaccessible at an air/water interface.

5. Concluding Remarks

The collapse kinetics of monolayer films can be expressed in transformation diagrams analogous to those employed for the phase transitions of cooled bulk materials. The C shape of $T\pi T$ diagrams reported here for POPC in the LE phase qualitatively predicts the behavior of the films, with the nose of the diagram indicating the existence of threshold compression rates for reaching otherwise inaccessible metastable states in which rates of collapse are negligible. The similar shapes of $T\pi T$ diagrams for POPC, and presumably for other liquid PC films that become metastable at high π , and the TTT diagrams of some liquid bulk materials suggest a similar basis for the analogous behaviors.

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Figure 1.

Area-decay of POPC monolayers at different constant surface pressures (π) above π_e . Measurements were obtained with a captive bubble after applying a fast compression, during which collapse is negligible, from equilibrium conditions below π_e to the different target π . Interfacial area (A) is normalized relative to the value (A_0) obtained when the film first reaches the desired π , which is subsequently held constant through feedback control. (a) Different π reached and kept constant within experimental error. (b) Area-decay of the films at the π shown in (a), with the same symbols indicating data from the same experiment. The measurements at 69 mN m^{-1} were omitted from subsequent analyses because a significant portion of the change in area might result from viscoelastic relaxation rather than collapse (see text). These data have been published previously.¹¹

Figure 2.

Schematic illustration indicating the use of hypothetical experimental data (top panels) to construct transformation diagrams (bottom panels). (a) TTT plot for bulk materials. T_c is the transition temperature and ξ is the fraction of the system transformed to the new phase at temperatures (T) below T_c . (b) T π T plot for monolayer collapse. A is the interfacial area, A_0 is the value of A when π first becomes constant and collapse is negligible, and π_e is the equilibrium spreading pressure. $(1 - A/A_0)$ is a measurement of the fraction of the film that has collapsed at π above π_e . Note that, unlike Figure 1, time, t , is plotted on a logarithmic scale.

Figure 3.

Schematic showing construction of CCT and CCpT plots. (a) CCT plot for bulk materials. The curves labeled as 1 and 2 show the traces of two different hypothetical continuous cooling paths in the plots of temperature (T) vs $\log(t)$. The CCT is obtained during continuous cooling at different rates from the locus of points for which the material has transformed by ξ . (b) CCpT plot for monolayer collapse. The traces of two continuous compression paths are labeled 1 and 2. The locus of points corresponding to a fixed percentage of area-reduction forms the CCpT.

Figure 4.

Determination of reduction in area (ΔA) caused by collapse from experimental isotherms for monolayers of POPC.¹¹ All experiments started at an initial π of approximately 46 mN m^{-1} , and time was measured relative to the initial time (t_0). Changes in area during fast compressions were assumed to result only from the film's compressibility. The isotherms for the fast compression used a linear fit ($r^2 = 0.9994$) to data from five experiments. (a) For T π T diagrams, ΔA is the difference between the area reached when the fast compression first achieves the target surface pressure (A_0) and the area at time t (A). (b) For CCpT diagrams, ΔA is the difference between the area that the film would have reached during a fast compression (A_0) and the area achieved at time t (A).

Figure 5.

$T\pi T$ diagram for POPC. (a) $T\pi T$ plot for 5% area-reduction, showing the experimental dispersion of individual measurements as well as the average values. (b) $T\pi T$ plots for 5, 10, 15, and 20% area-reduction, considering only average values.

Figure 6.

π - A isotherms for POPC obtained with continuous rates of compression. Measurements were obtained during compression of the bubble's volume (V) at constant rates, $(1/V_0)(dV/dt)$, normalized with the initial volume (V_0) under equilibrium conditions at 46 mN m^{-1} . During the measurements, rates of area-reduction changed with time. Rates indicated for each curve are therefore volume-reduction rather than area-reduction. The initial rates at which area changed, measured during the first 5 s for the slower compressions and the first 0.2 s for the fastest, were -0.11 , -0.25 , and -23 min^{-1} . For comparison, compression on a Langmuir trough at $1.2 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ of a film with an initial area per molecule of $60 \text{ \AA}^2 \text{ molecule}^{-1}$, which is the approximate area occupied by POPC at 46 mN m^{-1} , corresponds to an initial rate of 0.02 min^{-1} . These data have been published previously.¹¹

Figure 7. CCpT plot for 5% collapse of POPC monolayers. (a) Experimental dispersion of individual measurements and average values for CCpT. (b) Comparison of T π T and CCpT average plots.