RHEOPHYSICS OF LAMELLAR PHASES

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RHÉOPHYSIQUES DE PHASES LAMELLAIRES

Nous avons développé plusieurs techniques pour étudier l'effet du cisaillement sur des fluides complexes. Ces techniques sont basées sur des cellules de cisaillement spécialement adaptées aux techniques de dispersion ou aux propriétés de transport. Une courte description des cellules sera donnée en même temps que les résultats qui ont pu être obtenus en utilisant ces techniques. Des exemples sur les systèmes lyotropes seront décrits en détail.

L'effet du cisaillement sur des phases lamellaires lyotropes est étudié par diffusion de la lumière, diffusion de neutrons et observation microscopique. Nous avons constaté trois états différents d'orientation séparés par des transitions hors d'équilibre. Dans l'état à très faible gradient de cisaillement, la phase lamellaire est, en moyenne, orientée avec les couches dans le plan de cisaillement et quelques dislocations restent dans le sens de l'écoulement. Dans l'état intermédiaire, les couches s'organisent elles-mêmes en vésicules multicouches monodispersées (MLV) dont la taille est contrôlée par le gradient de cisaillement. Le dernier état correspond à la même orientation que la première, mais avec absence de dislocation dans le sens de l'écoulement.

Le deuxième état d'orientation conduisant à la structure MLV est plus précisément étudié. Il est montré que la taille des MLV est déterminée par un équilibre entre les efforts visqueux et élastiques et varie en fonction de l'inverse de la racine carrée du gradient de cisaillement. Un mécanisme possible pour la formation de cette structure est proposée. Nous montrons que cette structure peut être gonflée dans un solvant conduisant à une émulsion monodisperse d'une structure lamellaire dans un liquide isotope.

Les propriétés rhéologiques linéaires et non linéaires sont mesurées et discutées. On montre que la viscosité est sensible à la structure et varie de plusieurs ordres de grandeur en fonction de la phase d'orientation dans laquelle le système se trouve. Les deux comportements rhéofluidifiant ou rhéoépaississant sont décrits et des explications en termes de transitions d'orientation sont données.

La découverte de l'instabilité — orientée vers MLV — est la base d'un processus très efficace conduisant à des microcapsules bien contrôlées constituées de tensio-actifs. De nombreuses applications de MLV produites par cette technique sont décrites, y compris des applications biologiques. En particulier, nous présenterons des résultats sur l'encapsulation d'enzymes et d'ADN.

RHEOPHYSICS OF LAMELLAR PHASES

We have developed several techniques to study the effect of shear on complex fluids. These techniques are based on shear cells specially adapted to scattering techniques or transport properties. A brief description of the cells will be given together with the results that can be obtained using these techniques. Exemples on lyotropic systems will be detailed.

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The effect of shear on lyotropic lamellar phases is studied by light scattering, neutron scattering and microscopic observations. We found three different states of orientation separated with out-of-equilibrium transitions. In the state at very low shear rate, the lamellar phase is, in average, oriented with the layers in the shear plane and a few dislocations remains in the direction of the flow. In the intermediate state, the layers organize themselves into monodisperse multilayer vesicles (MLV) whose size is controlled by the shear rate. The last state corresponds to the same orientation than the first one but with no dislocations in the flow direction.

The second state of orientation: leading to the MLV structure, is more precisely studied. It is shown that the size of the MLV is fixed by a balance between the viscous and elastic stresses and varies as the inverse square root of the shear rate. A possible mechanism for the formation of this structure is proposed. We show that this structure can be swollen in a solvent leading to a monodisperse emulsion of a lamellar structure in an isotropic liquid.

Linear and nonlinear rheological properties are measured and discussed. It is shown that the viscosity is sensitive to the structure and varies of several order of magnitude depending in which phase of orientation the system is. Both shear thickening and shear thinning are described and explanations in terms or orientation transitions are given.

The discovery of the oriented to MLV instability is the basis a very efficient process leading to well controlled microcapsules made of surfactant. Many applications of MLV produced by this technique are described including biological ones. In particular we will present results on enzymes and DNA encapsulation.

REOFÍSICAS DE FASES LAMINARES

Hemos desarrollado ya diversas técnicas destinadas a estudiar el efecto de cizallamiento en los fluidos complejos. Estas técnicas se fundan en células de cizallamiento especialmente adaptadas a las técnicas de dispersión o a las propiedades de transporte. Figura en este artículo una corta descripción de las células, al mismo tiempo que los resultados que se han podido obtener por utilización de estas técnicas. Se describirán con más detalle varios ejemplos acerca de los sistemas liotropos.

El efecto de cizallamiento en las fases laminares liotropas se estudia por difusión de la luz, difusión de neutrones y observación microscópica. Hemos podido comprobar tres estados diferentes de orientación separados por transiciones fuera de equilibrio. En el estado de gradientes sumamente reducido de cizallamiento la fase laminar está, en promedio, orientada hacia las capas en el plano de cizallamiento y algunas dislocaciones subsisten en el sentido de la circulación. En el estado intermedio, las capas se organizan por sí mismas en vesículos multicapas monodispersas (MLV) cuya dimensión se encuentra controlada por el gradiente de cizallamiento. El último estado corresponde a la misma orientación que la primera, pero con inexistencia de dislocación en el sentido de la circulación.

El segundo estado de orientación que conduce a la estructura MLV se estudia con mayor detalle. Se demuestra que la dimensión del MLV se determina por un equilibrio entre los esfuerzos viscosos y elásticos y varía en función de la raíz cuadrada inversa del gradiente de cizallamiento. Se propone un mecanismo posible para la formación de esta estructura. Por nuestra parte, tratamos de demostrar que esta estructura puede aumentar de volumen en un disolvente que conduce a una emulsión mondispersa de una estructura laminar en un líquido isótopo.

Las propiedades reológicas lineales y no lineales se miden y se ponen en discusión. Se demuestra que la viscosidad es sensible a la estructura y varia según varios órdenes de magnitud en función de la fase de orientación en la cual se encuentra el sistema. Ambos comportamientos se reofluidifican o se reoespesan figuran descritos y también figuran las explicaciones en términos de transición de orientación.

El descubrimiento de la inestabilidad – orientada hacia MLV – constituye la base de un proceso sumamente eficaz que conduce a microcápsulas perfectamente controladas compuestas por tensioactivos. Se describen las numerosas aplicaciones de MLV producidas por esta técnica, e inclusive las aplicaciones biológicas. En particular, presentamos los resultados por encapsulado de enzimas y de ADN.

Studying the effect of shear on systems having a large characteristic length allowed us to relate the effect of shear to the microstructure. Typical systems studied are either near a second order phase transition [1] and [2], or colloidal systems [3] and [4]. One basic issue of these works is to understand the viscoelastic behavior of fluids in terms of microstructure, in the same way that statistical mechanics allows to describe the stability and the thermodynamics of equilibrium systems.

We have studied the effect of shear on a lyotropic lamellar phase. We have been able to show that the orientation taken by a lyotropic lamellar phase under shear can be described as steady states separated by transitions as a function of the characteristic distance between membranes and the shear rate [5]. Three different states of orientation of the lamellar phase have been described: an isotropic state where the membranes form onion-like structures (multilayer spherical objects of size R much larger than the repeating distance d) exists at intermediate shear rates in between two other states (at either lower or higher shear rates) where layers are mainly parallel to the flow. The location of these regions in the shear rate/smectic-period plane has been called the shear diagram [5] (see Fig. 1).

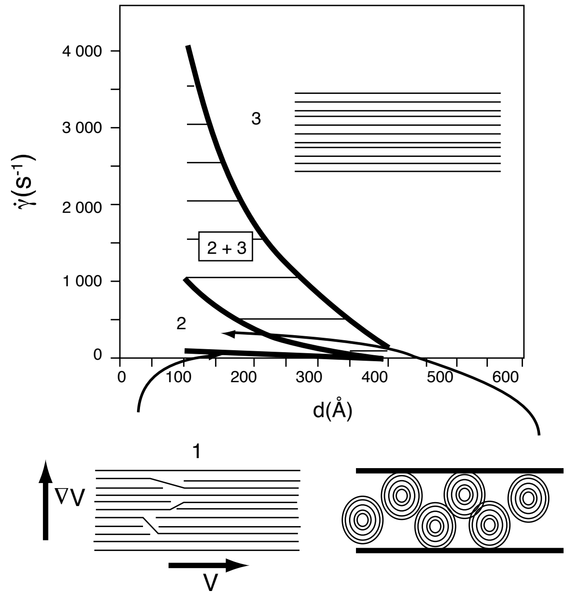

Figure 1

Shear diagram of the SDS/pentanol/dodecane/water lamellar phase. Three different stationary states of orientations are described.

We also have studied the consequences of the so-called shear diagram on the rheological properties of a lyotropic lamellar phase. Studying the shear rate as a function of the stress we have shown that the passage from one state to the other corresponds to out-of-equilibrium transitions. The first transition can be either discontinuous or continuous depending upon the repeating distance when the second transition seems to be always discontinuous. Approaching the bifurcation point where the first transition goes from continuous to discontinuous we show that oscillation in time may be observed. We interpret this behavior as due to a coupling between transitions and emphasize the fact that rheological behavior has to be described within the framework of dynamic transition rather than static ones.

A lyotropic lamellar phase made of water, Sodium Dodecyl Sulfate (SDS), pentanol and dodecane exhibiting a lamellar phase whose repeating distance lies between 60Å to 400Å [6] has been studied. This phase corresponds to layers of water surounded with surfactant separated with dodecane. It is stabilized by undulation interactions [7]. Using Couette cells and different techniques, we have shown that a shear diagram can be described corresponding to different orientations of the smectic layers respecting the flow field [5] (see Fig. 1). This diagram exhibits three states of orientation as shown in ref. [5]. At very low shear rates ($\dot{\gamma} < 1\ s^{-1}$) and high surfactant concentrations, the membranes are mainly parallel to the flow with the smectic director parallel to the velocity gradient direction (region 1). In this state a lot of defects (probably dislocations) persists in the two directions perpendicular to the director. It is presumably similar to the one described by Oswald and Kléman for thermotropic systems [8]. At higher shear rate or for more dilute systems, a new state appears where the smectic layers (membranes) form multilayer spherical droplets of well defined size, controlled by the shear rate, ranging typically from 10 mm to less than 1 mm (region 2) [5] and [9]. At even higher shear rates, a state where the membranes are parallel to the flow with the smectic director parallel to the gradient of velocity direction is stable. This state has some similarities with the first one but no defects remains in the direction of the flow (region 3). When observations are made in a cell where the shear rate is fixed, regions 2 and 3 are separated with a region where the two states coexist (region 2+3).

In order to get informations on the rheology, experiments have been made with a Rheometer Carrimed 100 that fixes the stress and measures the velocity (shear rate). We have used a Mooney cell corresponding to a Couette cell ended by a cone/plate at the bottom in order that the shear rate is uniform in all the cell. We have measured for different repeating distances the shear rate ($\dot{\gamma}$) as a function of the stress (S). Three regimes are described (see Fig. 2); corresponding to 3 different power laws ($S \propto \dot{\gamma}^{x}$). Regions 1 and 3 correspond to an exponent $x = 1$ when region 2 corresponds to $x = 0.2$. One sees that regions 1 and 3 correspond to a Newtonian behavior ($S \propto \dot{\gamma}$, viscosity: η = constant) but exhibit very different viscosities. Region 2 corresponds to a continuous shear thinning (viscosity decreasing with the shear rate $\eta \propto -0.8$). We also see that the passage from region 2 to region 3 corresponds to a jump in the shear rate for a given value of the stress when the passage from region 1 to 2 corresponds to either a jump in the stress (or viscosity) at constant shear rate or to a continuous process depending upon the dilution (see Fig. 2).

Let us first study the second transition between regions 2 and 3. When the stress at which the transition is reached (around 4 Pa for the 69% of oil sample and 50 Pa for the 50 %), a very small increase of the stress leads to a jump in shear rate to a rather larger value. For sample 69% the jump corresponds to an evolution of the shear rate from typically 200 s^{-1} to 900 s^{-1}. For sample 50% (2b) the jump starts at 1000 s-1 and ends above the maximum shear rate that the apparatus can measure (1200 s^{-1}). If measurements are made relatively rapidly (not waiting for the complete steady state equilibrium) one observes an hysteresis cycle. The white circles are obtained on the way up (increasing the shear rate) when the full dots corresponds to the way down (decreasing the shear rate).

The first transition is more complex (between states I and II). Indeed, for concentrated samples ($\phi_{oil} < 68\%$) the transition is discontinuous in stress when it becomes continuous for $\phi_{oil} > 68\%$. The transition between discontinuous ($D\eta \neq 0$) to continuous ($D\eta = 0$) transition is a bifurcation point (10).

The fact that these transitions are out-of-equilibrium in nature leads to a richer behavior that what is expected only from a description of stationary states. Indeed, in these transition, either feedback effects or coupling between transitions can lead to time evolutions which are no longer stationary but oscillations or chaotic behavior as a function of time are expected in certain cases. We may expect to find such states in the rheological behavior of these systems.

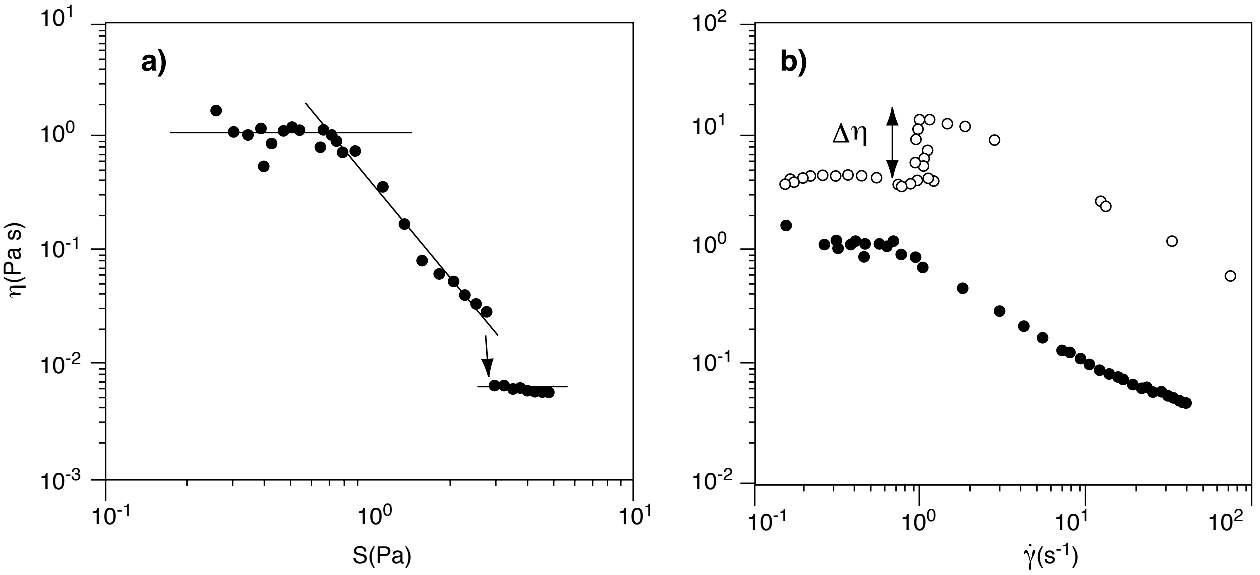

Figure 2

Evolution of the viscosity as a function of the shear rate along the shear diagram. The different states of orientations and the transitions are clearly observed.

a) a complete scan showing the three different states of orientations.

b) the transition between the oriented state and the onion state can be either continuous or discontinuous. In the latter case a shear thickenning effect is seen.

In conclusion, one would like to stress that the complicate behavior exhibited by the rheology of lyotropic smectic phase can be interpreted at a microscopic level as different states of orientation separated with out-of-equilibrium transitions.

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Final manuscript received in January 1997