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Complex propagation of surface waves on soft gels

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A spectroscopic study of surface waves was made on gels of gelatin and agarose over the frequency range 10^1–10^6 Hz. Two different optical techniques, the ripplon light scattering and the induced-surface-wave measurement were used for the appropriate frequency range. The dispersion curve determined for the gelatin gel showed that surface-tension waves appear in a frequency range higher than 20 kHz in spite of its solidity, while surface elastic waves propagate at frequencies lower than 300 Hz. As for the waves in the intermediate region, a theoretical prediction suggested coexistence of both waves though it was not confirmed experimentally. A similar result was obtained also in an agarose gel.

I. INTRODUCTION

Our previous study on gelatin[1] was to answer the question: Which type of surface wave, surface-tension wave or surface-elastic wave, propagates on gels which have mechanical properties somewhat intermediate between liquid and solid? We made light-scattering measurements of surface waves above 20 kHz and showed that the surface-tension wave occurs on gelatin gel in spite of its finite value of the shear elasticity.

Gel is a state in which colloid solution (sol) makes a very soft solid by constructing network structures of the solute molecules. In the sol-to-gel transition, fluidity of the solution is lost and shear elasticity emerges. Though we found that the surface of gel behaves like liquid above 20 kHz, we have little knowledge yet on its dynamic property at lower frequencies. It might happen that the shear elasticity works as a major restoring force which determines the wave propagation,[2] and the surface wave changes its mode from liquidlike to solidlike. This prediction is made from the fact that gel keeps a certain shape from a static point of view and behaves as a solid for slow movements. To settle this open question, we made the spectroscopic study of surface waves over a wide frequency range from 20 Hz to 800 kHz. We studied gelatin and agarose as well. Agarose gel has higher elasticity and lower viscosity than gelatin gel, and the effect of shear elasticity is expected to appear more explicitly.

The dispersion relation of the surface-tension wave is derived from the hydrodynamic theory as follows:[3]

$$(\Omega+2\nu k^2)^2-4\nu^2k^4\left[1+\frac{\Omega}{\nu k^2}\right]^{1/2}+(\sigma/\rho)k^3=0\ ,$$
$$\Omega=i\omega-\Gamma\ , \tag{1}$$

where ω is the angular frequency, Γ is the damping constant, k is the wave number, σ is the surface tension, ρ is the density of gel, and ν is the kinetic viscosity defined as $\nu=\eta/\rho$, η being the shear viscosity. This equation has an approximate solution giving the phase velocity proportional to the cubic root of the frequency:[4]

$$v\approx\left[\frac{2\pi\sigma}{\rho}f\right]^{1/3}\ . \tag{2}$$

On the other hand, the phase velocity of the surface-elastic wave is independent of f and given as,

$$v\approx 0.95(G/\rho)^{1/2}\ , \tag{3}$$

where G is the shear elastic modulus.

Equations (2) and (3) should be associated with a pure-mode wave on an ideal material with $G=0$ and $\sigma=0$, respectively. Actual gels possess finite values of both properties, however, which would have a contribution to the wave propagation depending on k. Here we discuss the crossover region where they have a comparable contribution. The particle motion of surface waves is localized in the subsurface layer with depth $\sim 1/k$. The mean strain induced by the surface-elastic wave with amplitude a is roughly estimated to be ak, which applies a driving force $F_E\sim akG$ to a unit volume. On the other hand, the surface-tension wave applies a driving force which is proportional to σ and the curvature of the surface: The force per a unit surface area is given by $F_S\sim ak^2\sigma$. By equating these two forces, we can get the crossover wave number

$$k=G/\sigma\ . \tag{4}$$

The corresponding crossover frequency is then derived from Eq. (2) or Eq. (3) as

$$f_C=\frac{1}{2\pi}\frac{G^{3/2}}{\sigma\rho^{1/2}}\ . \tag{5}$$

Equations (2) and (3) would be valid under the conditions $F_S>10F_E$ and $F_S<0.1F_E$, which lead to $k>10G/\sigma$ and $k<0.1G/\sigma$, respectively. We will calculate the crossover frequencies of the sample gels using the actual surface tension and shear elasticity, and experimentally examine them in a latter section.

II. EXPERIMENT

The samples used were gelatin and agarose, which are the typical material making hydrophysical gels. Gelatin powder (DIFCO Laboratories) was dissolved into the distilled water and stirred well at 50.0 °C. We prepared two solutions with concentrations 3.0 and 5.0 wt. %. The surface tension of the solution was measured by Wilhelmy method to 32.0 mN/m for both 3.0 and 5.0 wt. %. Measurements in sol state were done at 30.0 °C. Gelation was not observed at this temperature. Then the sol was cooled down for gelation and kept at 20.0 °C for more than 20 h until no change was observed in the surface-wave propagation. Agarose powder (WAKO Chemical) was also dissolved into the distilled water at above 90 °C, and a 0.50 wt. % solution was made. The measurements in sol and gel states were made at 50.0 °C and 20.0 °C, respectively. The gelation of this solution took place much faster than gelatin, and no change was observed 3 h after the cooling. These samples showed no substantial change in their volume through the gelation process and the densities were 1.0×10^3 kg/m^3 for all the samples.

We used two optical methods of surface-wave spectroscopy: the ripplon light-scattering technique in the frequency range from 20 k to 800 kHz,[5] and the induced-surface-wave technique in the range from 20 to 10 kHz.[6] Both of them have been reported in detail elsewhere and brief descriptions are given here. In the light-scattering method, laser light is directed normally to the surface and scattered by ripplons (thermally excited surface waves). The optical heterodyne technique gives the power spectrum of the scattered light with very high resolution. Frequency of the surface wave is obtained from the spectrum, while the wave number is obtained from the scattering angle. As for gelatin gel, frequency and damping constant of the surface wave were accurately measured up to 800 kHz. These specimens are perfectly transparent at the laser wavelength (514.5 nm) and local heating effect by the laser power was not observed.

The induced-surface-wave technique generates the waves by up-and-down vibration of a thin gold wire driven by electromagnetic effect. The minimum wavelength that can be induced is approximately estimated to be twice the wire diameter, which is equal to 50 μm. It corresponds to 50 kHz in gelatin gel. Detection of the surface wave is done by measuring the deflection of a probe laser beam normally incident to the surface. The shortest wavelength detected is equal to twice the spot diameter of the laser, and it is also 50 μm. This technique would have a potential ability to cover frequency range well up to the light-scattering region but for the Joule heating effect. The ohmic loss of the wire heated up the gelatinized specimen and locally melted it in the continuous wave driving even if the amplitude was kept below a certain level. To avoid this troublesome effect, we could not but reduce the average input power by a pulse mode operation. The consequence was that we could not take the advantage of a lock-in amplifier, which otherwise would have provided us with very high sensitivity in the detection. The strong attenuation of the surface waves on gels also decreased the signal intensity, and the highest measurable frequency was restricted below 4 and 15 kHz in gelatin gel and agarose gel, respectively.

III. RESULTS

Gelatin

Figure 1 shows some examples of power spectra of the light scattered by the surface wave on gelatin sol and gel (5.0 wt. %) at different scattering angles. The peak frequency and half width at half maximum of the spectra give the frequency and the temporal damping constant of the surface wave, respectively. The signal intensity is much smaller in gel than in sol, though it has the same height in the figure. One notable feature is found in these spectra: The peak is almost at the same frequency both in sol and gel state. It suggests that the phase velocity of the surface wave does not change in the gelation process even though the shear elasticity emerges. Figure 2(a) shows the phase velocity of 5.0 wt. % gelatin sol and gel obtained from the peak of the fitted curves. The solid line shows the dispersion relation of the surface-tension wave at $\sigma = 32$ mN/m, and the dashed line shows the extrapolation of the observed data at the low-frequency limit. The phase velocity in sol increases in proportion to cubic root of the frequency throughout the range of measurement, as expected from the theory of Eq. (2). The curve of gel shows somewhat different feature, however. In the range above 20 kHz, the phase velocity has almost the same value and the same frequency dependence as sol indicating that the dominant restoring force of the surface wave is the surface tension, and the shear elasticity has a negligible effect on the surface-wave propagation. Note here that the temperature dependence of surface tension is generally very small, and actually the difference in the phase velocity between 20.0 and 30.0 °C is smaller than the measurement error.

One could also find that the width of the power spectra

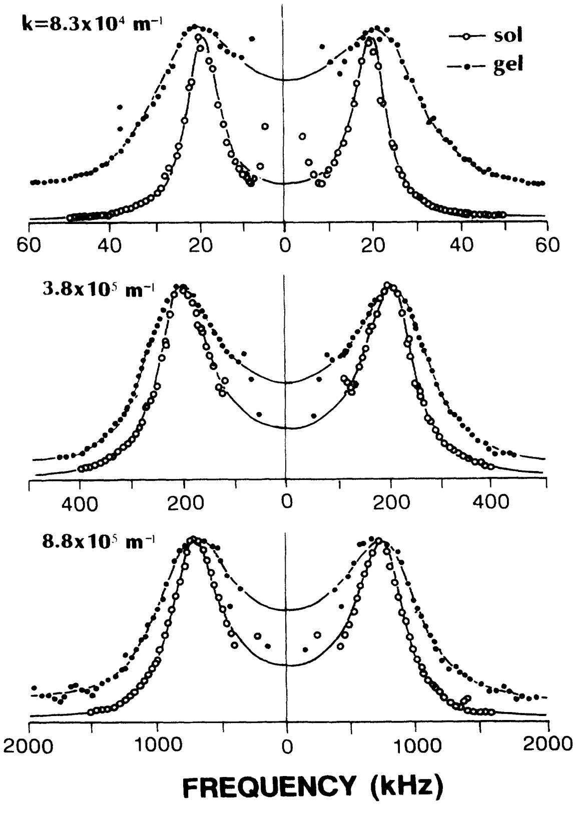

FIG. 1. Typical power spectra of ripplon light scattering obtained in 5.0 wt. % gelatin solution. The open and closed circles indicate the results for sol and gel, respectively.

of gel is larger than that observed in sol. It implies that the ripplon damping increases through the gelation process. The shear viscosity of the gelatin solution is known to increase as the network structure is formed in the solution and the present results agree with the previous experiments.[7] A detailed discussion on ripplon damping has been given in our previous paper.[1]

At lower frequency range below 300 Hz, however, the curves of gel and sol are quite different from each other: The phase velocity is much higher in gel than in sol and almost independent of frequency. It suggests that the nondispersive Rayleigh wave (surface-elastic wave) propagates in this lower frequency range. This region of surface-elastic wave transfers to the region of surface-tension wave through the intermediate region where both the surface tension and the shear elasticity may have a comparable contribution to the wave propagation. A similar feature of phase velocity was observed also in 3.0 wt. % solution as shown in Fig. 2(b), though the difference between gel and sol was less clear.

The shear elasticities of gelatin gels were obtained from Eq. (3) with the low-frequency limit of the wave velocity: They are 760 and 190 Pa for the samples of 5.0 and 3.0 wt. %, respectively. The crossover frequencies were then obtained from Eq. (5) as 3.5 kHz for 5.0 wt. % and 440 Hz for 3.0 wt. %. These values are in good agreement with the crossover frequency appearing in Fig. 2.

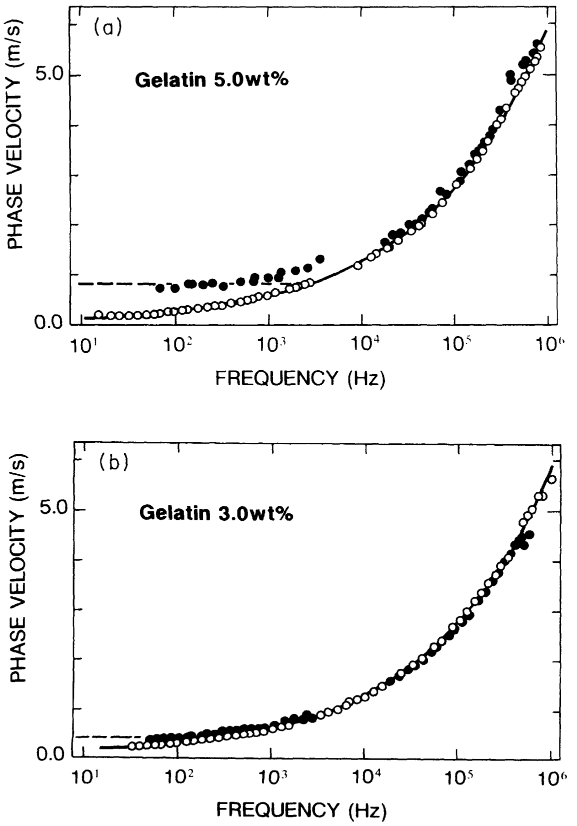

FIG. 2. Velocity dispersion of surface waves observed in gelatin sol (open circles) and gel (closed circles) at (a) 5.0 wt. % and (b) 3.0 wt. %. The solid and dashed lines represent the dispersion of the surface-tension wave and surface-elastic wave, respectively.

The dispersion curves of sol and gel overlap each other in the high-frequency region, suggesting that the surfaces of gel have the same surface tension as those of corresponding sol. Surface tension is generally determined by the number of solute molecules adsorbed onto the surface. Molecules of gelatin forms micelles in the solution at concentrations higher than the critical micelle concentration (CMC), which is about 0.2 wt. % at 35 °C.[8] It implies that density of free monomers in the solution, which is in equilibrium with the density of surface adsorption, is saturated above CMC. The surface tension of the present specimens, which are much thicker than CMC, is almost independent of the bulk concentration. In the gelation process, networks are constructed of solute molecules, which are effectively supplied by the micelles in the solution: The gelation does not change the monomer density and, hence, the surface density. It is thus natural that the surface tension of the gel has the same value as the sol in this specimen. High-frequency measurement of the surface wave would offer a new means to measure the surface tension of soft gel.

Agarose

Dynamic properties of agarose gel are more elastic than those of gelatin. The measurable frequency of the light-scattering method was restricted below 300 kHz due

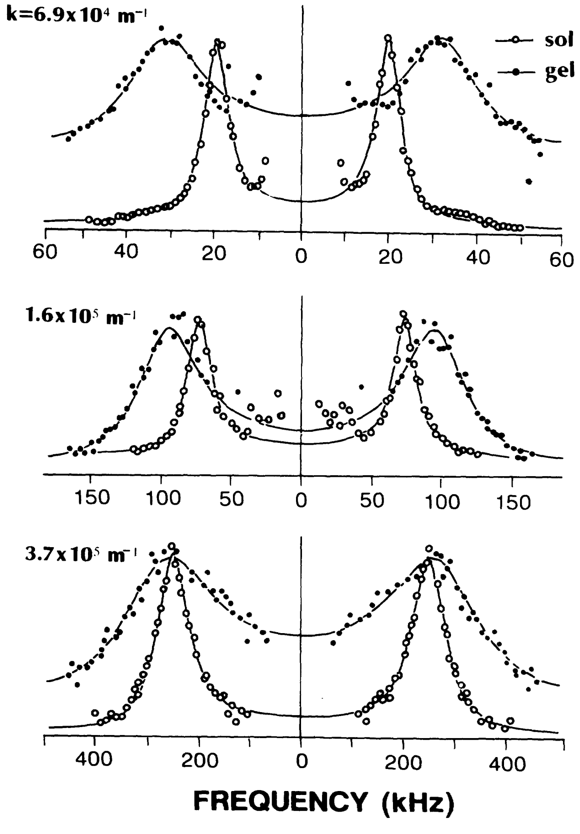

FIG. 3. Typical power spectra of ripplon light scattering obtained in agarose solution at 5.0 wt %, in which the open and the closed circles correspond to the spectrum of sol and gel, respectively. At low wave numbers, the ripplon peak shows a substantial shift in the gel-to-sol transition.

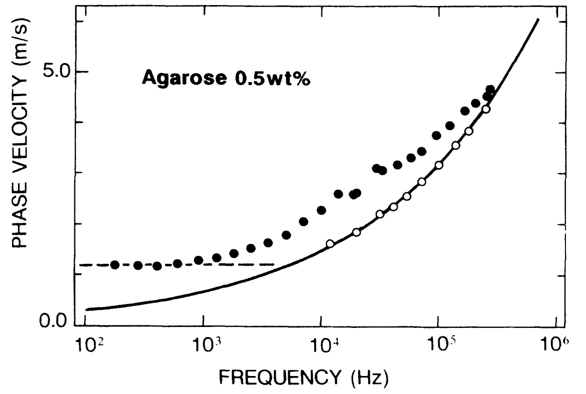

FIG. 4. Velocity dispersion of surface waves on agarose sol (open circles) and gel (closed circles). The solid and dashed lines represent the dispersion of the surface-tension wave and surface-elastic wave, respectively.

to the small signal intensity of the scattering spectrum. Some examples of the power spectra obtained in agarose gel and sol at different wave numbers are given in Fig. 3, which shows a remarkable contrast to the spectra in gelatin. At lower wave number, the peak frequency of the curve is substantially higher in gel than sol. The difference gradually decreases with wave number, however, and the peak sites almost agree at $k = 3.7 \times 10^5\ \mathrm{m}^{-1}$. Phase velocities determined from these spectra are shown in Fig. 4 together with the results of induced-surface-wave method. The Rayleigh-wave region in which the phase velocity is independent of frequency appears below 1 kHz. The velocity gradually increases above this frequency, but the increase is slower than cubic root of frequency suggesting that the wave is in the intermediate region. The typical surface-tension-wave region would have been revealed if a light-scattering experiment well above 300 kHz was possible.

The shear elasticity was determined to 2591 Pa from the low-frequency limit of the wave velocity, while the surface tension was determined to be 50 mN/m from the high-frequency limit. The crossover frequency is then calculated to 13.3 kHz.

IV. DISCUSSION

The present experiments made in gelatin and agarose clearly showed an interesting fact that surface-elastic waves appear on gels at low frequencies, while surface-tension waves appear in the high-frequency range; and that each range depends on the shear elasticity of the material. Note that these two wave modes have completely different manner of particle motion at subsurface region; clockwise circle of surface-tension wave vs counterclockwise ellipsoid of elastic wave. We encounter here another question of interest: What would the intermediate region be like where the surface tension and the elasticity have a comparable contribution to the wave propagation? There would be two possible answers to this question: The two forces work in harmony to generate one hybrid surface mode; or two wave modes propagate independently on each other. For further understanding of this problem, we have started an analysis of its theoretical aspect: We are trying to approach the region of interest down from the surface-tension region. Equation (1) which gives the dispersion relation of the surface-tension wave was modified so that it can take the effect of shear elasticity into account.[9] The kinetic viscosity ν was replaced with a complex kinetic viscosity $\nu^* = (\eta' - i\eta'')/\rho$, where $\eta'' = G/\omega$. A numerical work on this modified equation with appropriate values of G, σ, and η' yields two solutions which seem to lead to different dispersion curves, one for a quasi-surface-elastic wave and the other for a quasi-surface-tension wave. The theoretical consideration thus makes a prediction against the propagation of one hybrid wave mode but for the coexistence of two independent modes. Then the next step we should take is to observe the two surface wave propagating simultaneously. If they appear in the frequency range of the light-scattering experiment (above 20 kHz), the power spectrum of the scattered light would have a complicated shape with double peak, reflecting the different phase velocity of the two waves. The lowest curve of Fig. 3 actually has a shoulder which might be attributed to the second wave. Anyway, observation of two clear peaks would be seriously prevented by the strong attenuation which broadens these peaks.

On the other hand, Fig. 2(a) suggests that the region of problem in gelatin gel is below 20 kHz, the region of the induced-surface-wave technique. In this method, the two coexisting waves would be observed as a pulse separation in a long-distance propagation. Unfortunately, our measurement of phase velocity determined the propagation time from the delay of one particular phase point in a traveling pulse. If the pulse is the superposition of two waves with different velocity, the phase point would lose a correct meaning and, perhaps, give a velocity somewhat in between. Figure 2(a) shows a very slow increase above 1 kHz, which might be explained with the ambiguity of the present experiment.

In conclusion, the present experiment answered one question but raised another. This problem of an intermediate region would be solved by the study of intensive and careful experiment with the theoretical prediction in its scope. As for the induced wave method, the pulse separation or distortion could be clearly observed in a large trough which allows a longer propagation distance. The power spectrum of the light scattering should be fitted to a theoretical curve taking the effect of the two waves into consideration. We are preparing for this next stage of experiment, of which the result will soon be given.

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