Absence of surface mode in a viscoelastic material with surface tension

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The surface waves in the viscoelastic media with the surface tension are studied using the Voigt-Kelvin model of the viscoelasticity. It is shown that the surface mode of oscillation does not exist in the parameter region where the effect of surface tension is larger than that of the elastic stress at the surface unless the viscous stress masks the elastic stress in the bulk. In the region, the surface oscillation is suppressed and the oscillation beneath the surface diffuses after the pulse goes into the bulk. The experimental relevance of the present results is also discussed. [S1063-651X(98)12412-1]

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Surface modes of oscillation in a material are quite different from bulk modes due to the boundary condition at the surface. In an elastic material, the longitudinal and the transverse modes are mixed in the Rayleigh mode (surface mode), and its speed is slower than both of them. As for the fluid where only restoring force is the surface tension, the dispersion of the surface wave is not linear but given by $\omega \propto k^{3/2}$. The transition between the two modes in the viscoelastic material like polymer solutions or gels has been studied theoretically [1–3] and experimentally [4–9].

The characters of these two modes, however, are quite different and they cannot mix easily in a viscoelastic material where both the elastic and the surface tension operate. It has been expected that the spectral peak of the surface tension wave in the thermal fluctuation does not transform into the Rayleigh peak smoothly but the two peaks tend to co-exist in the transition region, and the spectral structure should not be simple [2]. The expected shoulder structure of the spectral peak has not been observed clearly but the substantial increase of the spectral width was demonstrated in the transition region for polymer solutions upon increasing density [6,7]

Recently, a careful experiment was done to measure the speed and the attenuation of the *externally excited* surface wave in the sol and the gel phase of tungstic acid [10], which undergoes a sol-gel transition upon decreasing pH, and it was shown that there is an anomalous behavior around the sol-gel transition point; the wave speed rises sharply and then drops discontinuously, and the attenuation rate has a sharp peak. These behaviors have not been expected by the previous theories.

Being motivated by the above experiment, we analyze the dispersion relation of surface modes of a viscoelastic material. We focus our attention to the experimental situation where the inverse of the surface wave frequency is much smaller than the structural relaxation time of the polymer network over the wavelength. Then the Maxwell type of viscoelasticity can be ignored and the Voigt-Kelvin viscoelasticity, in which the stress is the sum of the elastic and the viscous stresses, is a good model. Note that the Voigt-Kelvin

model does not become particularly bad around the sol-gel transition point because we are interested in the phenomenon with finite frequency and wavelength. The sol phase behavior is also obtained within this model by setting the elasticity zero.

With this model, we demonstrate that the surface mode does not exist around the region where the surface tension competes with the elastic stress.

We assume the viscoelastic material is occupied in the $z>0$ space and the surface is located at the x-y plane. The displacement field $\vec{u}(x,y,z,t)$ can be decomposed into the transverse part $\vec{u}_t$ and the longitudinal part $\vec{u}_l$ as

$$\vec{u}=\vec{u}_t+\vec{u}_l;\quad \vec{\nabla}\cdot\vec{u}_t=0,\quad \vec{\nabla}\times\vec{u}_l=0; \tag{1}$$

then the equations of motion for $\vec{u}_t$ and $\vec{u}_l$ can be expressed as

$$\rho\ddot{\vec{u}}_t=\left(E+\eta\frac{\partial}{\partial t}\right)\nabla^2\vec{u}_t, \tag{2}$$

$$\rho\ddot{\vec{u}}_l=\left[\frac{4}{3}\left(E+\eta\frac{\partial}{\partial t}\right)+\left(K+\zeta\frac{\partial}{\partial t}\right)\right]\nabla^2\vec{u}_l, \tag{3}$$

where the dot denotes the time derivative and ρ is the mass density, E and K are the shear and bulk modulus, and η and ζ are the shear and bulk viscosity, respectively. Using a potential function ϕ_l, the longitudinal displacement $\vec{u}_l$ can be expressed as

$$\vec{u}_l=\vec{\nabla}\phi_l; \tag{4}$$

then equation of motion (3) is expressed as

$$\rho\ddot{\phi}_l=\left[\frac{4}{3}\left(E+\eta\frac{\partial}{\partial t}\right)+\left(K+\zeta\frac{\partial}{\partial t}\right)\right]\nabla^2\phi_l. \tag{5}$$

The stress tensor σ_{ij} is given by

$$\sigma_{ij}=2\left(E+\eta\frac{\partial}{\partial t}\right)(\varepsilon_{ij}-\tfrac{1}{3}\operatorname{Tr}[\varepsilon]\delta_{ij})+\left(K+\zeta\frac{\partial}{\partial t}\right)\operatorname{Tr}[\varepsilon]\delta_{ij}, \tag{6}$$

where ε is the strain tensor

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$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right). \tag{7}$$

For simplicity, we take the incompressible limit, $K \to \infty$, which is good for the experimental situation where the surface wave speed under investigation is much slower than the longitudinal wave speed. Then we have

$$\nabla^2 \phi_l = 0 \tag{8}$$

and

$$\sigma_{ij} = 2\left(E + \eta \frac{\partial}{\partial t}\right)\varepsilon_{ij} + \rho \ddot{\phi}_l \delta_{ij}. \tag{9}$$

Now we examine the solution of the form

$$\vec{u}_t(x,z,t) = [-f'(z,t)/ik, 0, f(z,t)]e^{ikx}, \tag{10}$$

$$\phi_l(x,z,t) = \phi(t)e^{ikx-kz}, \tag{11}$$

assuming the physical quantities does not depend on the y coordinate and the y component of the displacement is zero. In Eq. (10), the prime denotes the derivative in z. The parameter k is the wave number in the x direction; $k > 0$ in order that the solution should be the surface mode. Then the equation of motion (2) is given by

$$\rho \ddot{f}(z,t) = \left(E + \eta \frac{\partial}{\partial t}\right)\left(-k^2 + \frac{\partial^2}{\partial z^2}\right)f(z,t). \tag{12}$$

The boundary conditions at $z = 0$ are

$$\sigma_{xz} = 0, \quad \sigma_{zz} = -\gamma \frac{\partial^2 u_z}{\partial x^2}, \tag{13}$$

where γ is the surface tension. These can be represented as

$$-[f''(0,t) + k^2 f(0,t)] + 2k^3 \phi(t) = 0, \tag{14}$$

$$2\left(E + \eta \frac{\partial}{\partial t}\right)[f'(0,t) + k^2\phi(t)] + \rho\ddot{\phi}(t)$$
$$= \gamma k^2[f(0,t) - k\phi(t)]. \tag{15}$$

If we assume the sinusoidal time dependence,

$$f(z,t) = f_0 e^{-\kappa z - i\omega t}, \quad \phi(t) = \phi_0 e^{-i\omega t}, \tag{16}$$

with

$$\kappa \equiv \sqrt{k^2 - \rho\omega^2/\mu(\omega)}, \quad \mu(\omega) \equiv E - i\omega\eta, \tag{17}$$

then, from (14) and (15), we obtain the equation to determine the dispersion relation,

$$\left(2k^2 - \frac{\rho\omega^2}{\mu(\omega)}\right)^2 - \gamma \frac{\rho\omega^2 k^3}{\mu(\omega)^2} = 4k^3\sqrt{k^2 - \frac{\rho\omega^2}{\mu(\omega)}}. \tag{18}$$

Note that the branch with the positive real part should be taken for the square roots in order that the mode should be localized around the surface.

It is easy to examine that this equation gives the Rayleigh wave dispersion $\omega = c_R \sqrt{E/\rho} \cdot k$ with $c_R = 0.9553$, for the
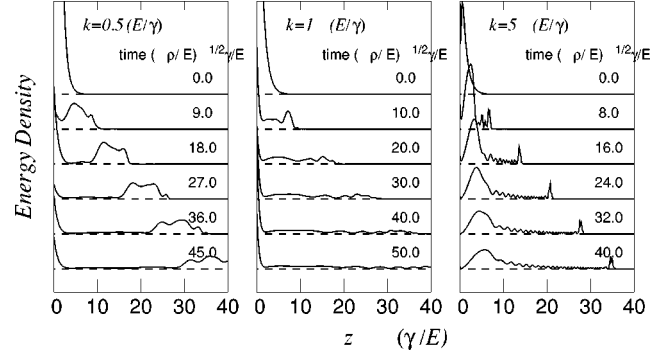

FIG. 1. Time developments of the oscillation for the $\eta = 0$ case. The energy density is plotted in an arbitrary unit against the depth z in the unit of (γ/E). The wave numbers in the x direction are $k = 0.5, 1$, and 5 (E/γ) and the initial states are given by Eq. (20) with $\lambda = 1, 0.5$, and $0.5(\gamma/E)$, respectively. The time is shown in units of $(\rho/E)^{1/2}\gamma/E$.

case of the elastic material ($E \neq 0$, $\gamma = \eta = 0$) and the capillary wave dispersion $\omega = \sqrt{\gamma/\rho}\, k^{3/2}$ in the case of the fluid ($\gamma \neq 0$, $E = \eta = 0$).

In order to see how the Rayleigh mode and capillary mode exclude each other, we consider first the case without the dissipation ($\eta = 0$, $E \neq 0$, and $\gamma \neq 0$); then Eq. (18) becomes

$$(2 - c^2)^2 - c^2\left(\frac{\gamma}{E}\right)k = 4\sqrt{1 - c^2}; \quad c \equiv \sqrt{\frac{\rho}{E}}\frac{\omega}{k}. \tag{19}$$

The dispersion relation is obtained by determining c for a given value of k. Again, note that the square root should have a positive real part.

This equation gives the Rayleigh wavelike dispersion for $k \lesssim E/\gamma$. In the case of $k > E/\gamma$, however, it does not have a solution in the physical branch of the square root. This means that there is no surface mode in the region of $k > E/\gamma$, where the capillary stress dominates.

In order to examine what is happening in the region without the surface modes, we solve the equation of motion (12) numerically with $\eta = 0$ under the boundary conditions (14) and (15) from the initial state given by $f(z, t = 0)$ localized around the surface within a length λ as

$$f(z, t=0) = f_0 e^{-z/\lambda}. \tag{20}$$

The time developments are shown in Fig. 1, where energy density

$$u_e = \sum_{i=x,z} \frac{1}{2}\rho\dot{u}_i^2 + \sum_{i,j=x,z} \frac{1}{4}E\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)^2, \tag{21}$$

is plotted as a function of z for $k = 0.5, 1$, and 5 (E/γ) with the initial configuration with $\lambda = 1, 0.5$, and 0.5 (γ/E), respectively. Note that the initial shape of u_e is not proportional to $(e^{-z/\lambda})^2$ because the longitudinal component given by Eqs. (4) and (11) decays as e^{-kz} in z.

It can be seen that the surface oscillation remains after the pulse is gone into the bulk for the case of $k = 0.5$ (E/γ), where the surface mode is allowed. On the other hand, the oscillation at the surface is strongly suppressed for k
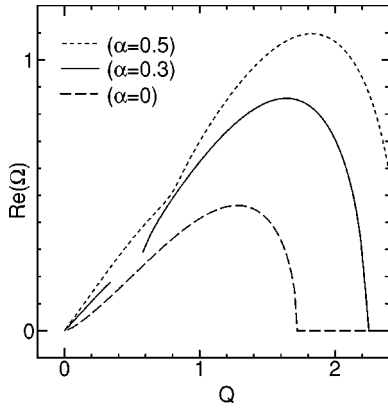
FIG. 2. Dispersion relations for $\alpha \equiv E(\eta/\gamma)^2/\rho = 0.5$, 0.3, and 0. The real part of $\Omega \equiv (\eta^3/\rho\gamma^2)\omega$ is plotted against $Q \equiv (\eta^2/\rho/\gamma)k$.

$= 5$ (E/γ), where the surface mode is not allowed. It is interesting to see, in this case, that there is a peak of oscillation just beneath the surface in addition to the pulse that travels into the bulk, and the peak of the oscillation diffuses away as the pulse goes in the bulk.

If the viscosity is introduced into the system, the situation becomes slightly more complicated. There takes place the competition among three stresses: the elastic stress, the surface tension, and the viscous stress. Depending upon which stress dominates, the mode character is expected to be one of the following: the Rayleigh mode, the capillary mode, or the overdamped liquid mode. In addition to these, however, there is the parameter region where no surface mode is allowed, as we have seen.

In Fig. 2, the result of the dispersion relation for $E = 0.5, 0.3$, and 0 $\rho(\gamma/\eta)^2$ is given; the real part of $\Omega \equiv (\eta^3/\rho\gamma^2)\omega$ is plotted as a function of $Q \equiv (\eta^2/\rho\gamma)k$. In the case of $E = 0.3\rho(\gamma/\eta)^2$, for small Q, the dispersion is linear and the mode is the Rayleigh wavelike, but for an intermediate value of Q, the mode becomes capillary wave-like, and for large Q, Ω becomes pure imaginary and the mode is the overdamped liquid mode. Between the elastic mode and the capillary mode, there exists the region where there exists no surface mode, namely, there is no solution for Ω on the physical branch of the square root in Eq. (18); we call it the ''gap region.''

The phase diagram in the E-k plane has been obtained numerically by calculating the dispersion from Eq. (18) [11], but the result is illustrated in Fig. 3 schematically. It can be understood as in the following way. The boundary between the Rayleigh mode and the overdamped liquid mode is determined by the competition between the elastic stress and the viscous stress, namely, $Ek|\vec{u}|$ and $\eta\omega k|\vec{u}|$, therefore the boundary is given by

$$k \sim \frac{1}{\eta}\sqrt{\rho E}, \qquad (22)$$

because $\omega \sim \sqrt{E/\rho} \cdot k$ in the Rayleigh mode region. Similarly, the boundary between the capillary wave and the overdamped liquid mode is given by

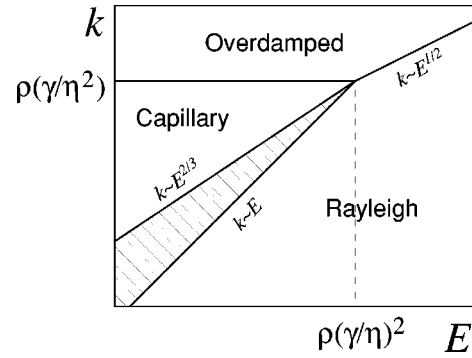$$k \sim \rho\gamma/\eta^2. \qquad (23)$$

FIG. 3. Schematic phase diagram in the E-k plane in the logarithmic scale. The shaded region is the gap region, where the surface wave does not exist.

It is instructive to examine how the gap region arises between the Rayleigh and the capillary region. For small enough k, the elastic stress dominates and the surface wave is Rayleigh like. For $E < \rho(\gamma/\eta)^2$, upon increasing k, the surface tension becomes dominant at

$$k \sim E/\gamma, \qquad (24)$$

where the surface mode disappears as we have seen for the dissipationless case. As k increases further, the elastic stress is taken over by the viscous stress at

$$k \sim \left(\sqrt{\frac{\rho}{\gamma}}\frac{E}{\eta} \right)^{2/3}, \qquad (25)$$

then the capillary wave emerges [12].

It is very suggestive that the existence of the capillary wave depends upon the competition between the elastic stress and *the viscous stress*, not the surface tension. No matter how large the surface tension is, the capillary wave is not allowed under the existence of elastic stress unless there exists the viscous stress. This can be explained as in the following: The mode characters of the two are too different to form a mixed mode, therefore, the Rayleigh wave dominates rather than mixes with the capillary mode when the elastic stress is larger. On the other hand, the capillary wave cannot overtake the Rayleigh wave even when the surface tension at surface is larger than the elastic stress because the surface tension operates only at the surface and the displacement field inside is governed by the elastic stress in the bulk. The viscosity, however, gives the capillary wave a chance to win by masking the effects of the elastic stress.

The overdamped liquid mode under the existence of the surface tension is also worth mentioning: In the bulk, it has the dispersion

$$\omega = -i\frac{\eta}{\rho}k^2. \qquad (26)$$

As for the surface mode, there is a similar overdamped mode with the dispersion

$$\omega = -i\frac{\eta}{\rho}c_R k^2 \qquad (27)$$

with the same constant c_R than the Rayleigh wave, and this is the only one in the case without the surface tension. With the surface tension, however, there appears another mode, the damping rate of which is smaller than the other's; the dispersion is given by

$$\omega \approx -i\frac{\gamma}{2\eta}k \tag{28}$$

for $k \gg \gamma\rho/\eta^2$.

Let us examine the experimental relevance of this gap region of the surface wave. In the recent experiment [10], it was reported that the surface wave shows anomalous behavior in the tungstic acid; sharp increase and discontinuous drop of wave speed and attenuation peak of the surface wave in the frequency range ~ 100 Hz have been observed around the sol-gel transition point, where the elasticity is very small and the Rayleigh wave speed is of the order of 0.1 m/s. Within the present framework, the sharp increase of the wave speed can be interpreted as the result of the group speed increase at the upper edge of the gap in the dispersion curve. The discontinuous drop of the wave speed and the large attenuation of the surface wave come from the suppression of the surface oscillation in the gap region.

The typical values of the parameters for the material are $\rho \sim 10^3$ kg/m^3, $\eta \sim 10^{-2}$ Pa s, $\gamma \sim 10^{-1}$ N/m. The elastic modulus changes rather rapidly around the sol-gel transition point, but $E \sim 10$ Pa in the region where the sound speed is 0.1 m/s, then the expected gap region is $k \approx 10^2 \sim 10^{3.3}$ m^{-1}, or $\omega \approx 10^1 \sim 10^{2.3}$ s^{-1}. This is consistent with the region where the anomaly is observed.

Before concluding, let us discuss possible effects of structural relaxation, which we ignore in the present work. The structural relaxation will relax part of the elastic stress for the longer time scale than its relaxation time τ_{st}, and can be expressed by the Maxwell model of viscoelasticity in a phenomenological level. If we include the effect, the capillary mode region would extend into the gap region to some degree on the small k side because the structural relaxation reduces the bulk elastic stress in a longer time scale than the structural relaxation time τ_{st}. The way that the gap region shrinks from the present result (Fig. 3) depends upon the detailed structure of the model and the relevant time scale; for $\omega \gg 1/\tau_{st}$ ($\omega \ll 1/\tau_{st}$), the part of the stress can be treated as elastic (viscous). The basic feature of the phase diagram, however, should not change as long as there exists a pure elastic component of the stress in the system as we assumed in the present study.

In summary, we found that, in the viscoelastic material, there is a parameter region where the surface mode is absent and it corresponds to the region where the surface wave anomaly is found in the recent experiment on tungstic acid [10].

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[12] The gap region is missing in the phase diagram Fig. 1 of [2], where the boundary between the capillary mode and the elastic mode is drawn.