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Roughness effect on the frequency of a quartz-crystal resonator in contact with a liquid

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The problem of coupling of the shear oscillations of a quartz crystal bounded by a rough surface with damped waves in a liquid has been investigated. The shift of the resonance frequency of a quartz crystal due to either random roughness or periodical corrugation has been considered. A relation between the shift and a correlation function of roughness has been found. It has been shown that the roughness effect is most pronounced in the low viscosity limit. It has been demonstrated that the results of quartz-crystal microbalance measurements can provide valuable information on the average height and the correlation length of surface roughness.

I. INTRODUCTION

A large number of experimental and theoretical studies have been devoted to the understanding of the dynamic properties of the solid-liquid interface. The topics of interfacial friction[1,2] and viscoelasticity[3] of thin surface layers are of importance in a wide range of problems related to surface wetting, film growth, phase transitions in adsorbed films, characterization of surface processes in electrochemical systems, polymer solutions, microemulsion, and so on. It was successfully demonstrated that the quartz-crystal microbalance (QCM) can serve as a sensitive tool to probe interfacial friction and viscoelasticity.[2,3] The shift of the quartz-crystal resonance frequency in various liquids has been studied in number of experimental works.[4,5] These experiments have generated theoretical attempts to describe the coupling of the crystal shear modes to a liquid motion. Different approaches[4,6,7] have been proposed to explain the dependence of a resonance frequency shift on bulk liquid density and viscosity. A common feature of all these approaches is the neglection of microscopic properties of interfaces and surface roughness.

Real surfaces are always characterized by specific roughness that depends on the material, method of surface treatment, and presence of adsorbed particles on the surface. It was shown experimentally[5,8–11] that surface roughness can drastically affect the resonance frequency. The authors of Refs. 8 and 9 attributed the effect of roughness to the additional mass of the solvent trapped in surface cavities. They concluded that changes in surface roughness during electrochemical oxidation are the dominant contributors to the observed frequency shift. The authors of Refs. 10 and 11 assumed that roughness can also increase energy dissipation in the liquid. The network analysis of the effect of roughness and interfacial liquid structure was presented in Ref. 5. Nevertheless, this subject is highly undeveloped.

In this paper we focus on the question of the influence of roughness on the resonance frequency of a quartz crystal. The problem of coupling of the shear oscillations of the crystal bounded by a rough surface with damped waves in the liquid is solved by the method of Rayleigh[12] and Fano.[13] A similar approach was used previously for the description of light scattering on a rough surface.[14,15] We consider here the effect of a randomly rough surface and a periodical corrugation. A relation between the resonance frequency shift and the correlation function of the roughness is derived. The roughness introduces a new length (a correlation length of roughness) within the continuum description of the liquid, and leads to viscosity and density dependencies that do not appear in the case of a smooth interface. It is demonstrated that the results of QCM measurements can provide valuable information about the average height and correlation length of surface roughness.

II. THE MODEL

We now consider a model for the coupling of shear waves in a piezoelectric crystal bounded by a rough surface with damped waves in a liquid. We plot a z axis pointing toward the liquid and the plane $z=0$ being coincident with the unconstrained face of the quartz resonator. We assume that the rough interface between the quartz crystal and liquid is described by the equation $z=\xi(x,y)$. The plane $z=d$ is chosen such that the average value of the function $\xi(x,y)$ over the surface is equal to zero. Here d is the average thickness of the quartz-crystal film.

For time-harmonic oscillations the elastic displacements $\mathbf{u}(\mathbf{r},t)=\mathbf{u}(\mathbf{r},\omega)\exp(i\omega t)$ in the crystal are described by the following wave equation:

$$-\omega^2\mathbf{u}(\mathbf{r},\omega)=\frac{\mu}{\rho_s}\nabla^2\mathbf{u}(\mathbf{r},\omega)\ . \tag{1}$$

Here μ and ρ_s are the shear modulus and the density of the quartz crystal, and ω is the frequency of oscillations. The fluid velocities $\mathbf{v}(\mathbf{r},\omega)$ are the solution of the linearized Navier-Stokes equation:

$$i\omega\mathbf{v}(\mathbf{r},\omega)=-\frac{1}{\rho_l}\nabla P(\mathbf{r},\omega)+\frac{\eta}{\rho_l}\nabla^2\mathbf{v}(\mathbf{r},\omega)\ , \tag{2}$$

where $P(\mathbf{r},\omega)$, η, and ρ_l are the pressure, viscosity, and density of the fluid. The velocities must also satisfy the incompressibility condition.

Boundary conditions for the elastic displacements and the fluid velocities include. (a) the absence of forces acting on the unconstrained crystal surface $z=0$; and (b) the equality of crystal and fluid velocities at the interface $z=\xi(x,y)$:

$$i\omega\mathbf{u}[x,y,z=\xi(x,y)]=\mathbf{v}[x,y,z=\xi(x,y)] \ . \tag{3}$$

Here we will solve the problem by means of the Rayleigh-Fano[12,13] perturbation theory which is valid for slightly rough surfaces. For such surfaces the characteristic size of the roughness in the z direction (the root-mean-square height), h, is less than the tangential one (correlation length) l. We will also assume that the height of the roughness is smaller than the decay length of fluid velocities, $\delta=(2\eta/\omega\rho_l)^{1/2}$, which is usually of the order of $0.1-1$ μm. The wavelength of shear-mode oscillations in the quartz crystal, $2\pi(\mu/\rho_s)^{1/2}\omega^{-1}$, is of the order of 0.1 cm, much larger than δ and l. As a result the presence of roughness discussed in this work does not influence the crystal oscillations. Hence the solution of Eq. (1) can be written in the following form:

$$\begin{aligned} &u_\alpha(\mathbf{r},\omega)=2C_\alpha\cos(kz) \ , \quad k=\omega(\rho_s/\mu)^{1/2} \ , \quad \alpha=x,y \\ &u_z(\mathbf{r},\omega)=0 \ . \end{aligned} \tag{4}$$

In order to solve Eq. (2) it is convenient to Fourier transform the fluid velocities, pressure, and roughness profile function $\xi(x,y)$ from the tangential coordinates $\mathbf{R}=(x,y)$ to the corresponding wave vectors $\mathbf{K}=(K_x,K_y)$ according to the equation

$$\xi(\mathbf{K})=\int d\mathbf{R}\,\xi(\mathbf{R})\exp(-i\mathbf{K}\cdot\mathbf{R}) \ . \tag{5}$$

The solution of Eq. (2) has the form

$$P(\mathbf{K},z,\omega)=P(\mathbf{K})\exp[-K(z-d)] \ , \tag{6}$$

$$\begin{aligned} \mathrm{v}_\alpha(\mathbf{K},z,\omega)=&\,A_\alpha(\mathbf{K})\exp[-q_K(z-d)] \\ &-\frac{1}{\rho_l\omega}K_\alpha P(\mathbf{K})\exp[-K(z-d)] \ , \quad \alpha=x,y \ , \end{aligned} \tag{7}$$

$$\begin{aligned} \mathrm{v}_z(\mathbf{K},z,\omega)=&\,\frac{i}{q_K}\sum_\alpha K_\alpha A_\alpha(\mathbf{K})\exp[-q_K(z-d)] \\ &-\frac{i}{\rho_l\omega}KP(\mathbf{K})\exp[-K(z-d)] \ . \end{aligned} \tag{8}$$

Here $K=|\mathbf{K}|$, $q_K=(i\omega\rho_l/\eta+K^2)^{1/2}$, and $\mathrm{v}_\alpha(\mathbf{K},z,\omega)$ and $\mathrm{v}_z(\mathbf{K},z,\omega)$ are the projections of the vector of velocity $\mathbf{v}(\mathbf{K},z,\omega)$ on the axes $\alpha=x$, y, and z, correspondingly.

The prefactors $A_\alpha(\mathbf{K})$ and $P(\mathbf{K})$ are obtained from boundary condition (3). Using Eqs. (4) and (6)–(8), and taking Fourier transforms of both sides of Eqs. (3), we obtain

$$\begin{aligned} \int\frac{d\mathbf{K}}{(2\pi)^2}&\left\{A_\alpha(\mathbf{K})\{\exp[-q_K\xi(\mathbf{R})]\}_{\mathbf{K}'-\mathbf{K}}-\frac{l}{\rho_l\omega}K_\alpha P(\mathbf{K})\{\exp[-K\xi(\mathbf{R})]\}_{\mathbf{K}'-\mathbf{K}}\right\} \\ &=i\omega C_\alpha\{\exp(ikd)[\exp(ik\xi(\mathbf{R}))]_{\mathbf{K}'}+\exp(-ikd)(\exp[-ik\xi(\mathbf{R})])_{\mathbf{K}'}\} \ , \end{aligned} \tag{9}$$

$$\int\frac{d\mathbf{K}}{(2\pi)^2}\left\{\frac{i}{q_K}\sum_\alpha K_\alpha A_\alpha(\mathbf{K})\{\exp[-q_K\xi(\mathbf{R})]\}_{\mathbf{K}'-\mathbf{K}}-\frac{i}{\rho_l\omega}KP(\mathbf{K})\{\exp[-K\xi(\mathbf{R})]\}_{\mathbf{K}'-\mathbf{K}}\right\}=0 \ . \tag{10}$$

In Eqs. (9) and (10) we introduced the following definition:

$$\begin{aligned} &\{\exp[-p\xi(\mathbf{R})]\}_{\mathbf{K}'-\mathbf{K}} \\ &\quad=\int d\mathbf{R}\exp[-p\xi(\mathbf{R})]\exp[-i(\mathbf{K}'-\mathbf{K})\mathbf{R}] \ . \end{aligned} \tag{11}$$

Coupled Eqs. (9) and (10) allow us to express coefficients $A_\alpha(\mathbf{K})$ and $P(\mathbf{K})$ through the amplitudes of shear waves in the crystal, C_α. We remark that the matrix elements of the kernel of these equations, of the type $(\exp[-q_K\xi(\mathbf{R})])_{\mathbf{K}'-\mathbf{K}}$ are not symmetric functions of $\mathbf{K}$ and $\mathbf{K}'$, since q_K' does not appear in the exponent.

After the determination of coefficients $A_\alpha(\mathbf{K})$ and $P(\mathbf{K})$ and, correspondingly, the fluid velocities $\mathbf{v}(\mathbf{r},\omega)$ the resonance frequency measured in quartz-crystal microbalance experiments can be found from the energy balance in the system under consideration. The rate of the change of the kinetic ($E_{\mathrm{kin}}^{(s)}$) and elastic (potential) ($U^{(s)}$), energy of the crystal, and the kinetic energy, ($E_{\mathrm{kin}}^{(l)}$), of the liquid should be equal to the rate of the energy dissipation in the liquid, $Q^{(l)}$,

$$\frac{d}{dt}(E_{\mathrm{kin}}^{(s)}+U^{(s)}+E_{\mathrm{kin}}^{(l)})=Q^{(l)} \ . \tag{12}$$

Here we neglect energy losses in the quartz crystal. The expressions for the energetic terms appeared in Eq. (12) have the form

$$E_{\mathrm{kin}}^{(s)}=\frac{\rho_s}{2}\int dR\int_0^{[d+\xi(\mathbf{R})]}dz\sum_i\left[\frac{\partial}{\partial t}\tilde{u}_i\right]^2 , \tag{13}$$

$$U^{(s)}=\frac{\mu}{4}\int dR\int_0^{[d+\xi(\mathbf{R})]}dz\sum_{i.j}\left[\frac{\partial\tilde{u}_i}{\partial r_j}+\frac{\partial\tilde{u}_j}{\partial r_i}\right]^2 , \tag{14}$$

$$E_{\mathrm{kin}}^{(l)}=\frac{\rho_l}{2}\int d\mathbf{R}\int_{[d+\xi(\mathbf{R})]}^{\infty}d\mathbf{z}\sum_i\tilde{v}_i^2 \ , \tag{15}$$

$$Q^{(l)}=-\frac{\eta}{2}\int d\mathbf{R}\int_{[d+\xi(\mathbf{R})]}^{\infty}dz\sum_{i,j}\left[\frac{\partial\tilde{v}_i}{\partial r_j}+\frac{\partial\tilde{v}_j}{\partial r_i}\right]^2 , \tag{16}$$

In Eqs. (12)–(16) we introduce the following notations:

$$\tilde{v}_i=\mathrm{Re}[v_i(\mathbf{R},z,\omega)\exp(i\omega t)]\ ,$$
$$\tilde{u}_i=\mathrm{Re}[u_i(\mathbf{R},z,\omega)\exp(i\omega t)]\ ,\quad \text{and}\quad i,j=x,y,z\ . \tag{17}$$

It should be noted that the energy balance equation (12) could be satisfied only for a complex resonance frequency $\omega_r=\Omega+i\Gamma$.

We will solve Eqs. (9) and (10) within the perturbation theory with respect to parameters $|\nabla\xi(\mathbf{R})|\ll 1$ and $h/\delta\ll 1$. At these conditions we can expand the matrix elements of the type $\{\exp[-q_K\xi(\mathbf{R})]\}_{\mathbf{K}'-\mathbf{K}}$ as

$$\begin{aligned}\{\exp[-q_K\xi(\mathbf{R})]\}_{\mathbf{K}'-\mathbf{K}} &=\delta(\mathbf{K}-\mathbf{K}')-q_K\xi(\mathbf{K}'-\mathbf{K})\\ &\quad+\tfrac{1}{2}q_K^2\int\frac{dK''}{(2\pi)^2}\xi(\mathbf{K}'-\mathbf{K}-\mathbf{K}'')\xi(\mathbf{K}'')+\cdots\end{aligned} \tag{18}$$

and solve Eqs. (9) and (10) by iterations. To determine the first non-negligible correction to the resonance frequency caused by roughness, we must find coefficients $A_\alpha(\mathbf{K})$ and $P(\mathbf{K})$ up to the second order with respect to the root-mean-square (rms) height of the roughness h. We remark that it is enough to obtain the second-order terms only for the zero value of the two-dimensional wave vector $\mathbf{K}$. To the lowest order we arrive at results for the smooth interface between the quartz crystal and the liquid:

$$A_\alpha^{(0)}(0)=2iC_\alpha\omega\cos(kd)\ ,\quad A_\alpha^{(0)}(\mathbf{K})=0\ ,$$
$$P^{(0)}(\mathbf{K})=0\ . \tag{19}$$

To the first and the second orders, we have

$$A_\alpha^{(1)}(\mathbf{K})=2i\omega q_0\cos(kd)\xi(\mathbf{K})\times\left[C_\alpha+\frac{K_\alpha}{K(q_K-K)}\sum_\beta K_\beta C_\beta\right]\ ,\quad \beta=x,y \tag{20}$$

$$P^{(1)}(\mathbf{K})=\frac{\rho_l\omega}{q_K}\frac{1}{K}\sum_\beta K_\beta A_\beta^{(1)}(\mathbf{K})\ , \tag{21}$$

$$A_\alpha^{(2)}(0)=-i\omega\cos(kd)\left\{\int\frac{d\mathbf{K}}{(2\pi)^2}|\xi(\mathbf{K})|^2\times q_0\left[C_\alpha(q_0-2q_K)-2\frac{K_\alpha}{K}\sum_\beta K_\beta C_\beta\right]\right\}. \tag{22}$$

Solving Eqs. (9) and (10) we neglect terms proportional to the factor $(k\xi(\mathbf{K}))$ compared to ones proportional to $(q_0\xi(\mathbf{K}))$ because of the inequality $k/q_0\ll 1$. After the substitution of the expressions (19)–(22) into Eq. (12), we find the resonance frequency ω_r up to the second order in the rms height of roughness:

$$tg(kd)+\frac{\rho_l}{\rho_s}\frac{k}{q_0}=-\frac{\rho_l}{S\rho_s}k\int\frac{d\mathbf{K}}{(2\pi)^2}|\xi(\mathbf{K})|^2[q_K-q_0+K\cos^2\phi]\ , \tag{23}$$

where S is the area of a crystal surface, and ϕ is the angle between the direction of shear oscillations and the two-dimensional (2D) vector $\mathbf{K}$.

At $\xi\equiv 0$, Eq. (23) gives the resonance frequency at a smooth crystal liquid interface.[4] The shift and broadening of the resonance due to the presence of the roughness is determined by the rms height h, and by the pair-correlation function $g(\mathbf{K})$. The last quantity is related to $|\xi(\mathbf{K})|^2$ as $|\xi(\mathbf{K})|^2=Sh^2g(\mathbf{K})$. Equation (23) can be used to describe the effect of both random roughness and periodical corrugation. In the last case we have just to substitute the integral $\int d\mathbf{K}/(2\pi)^2$ for the sum $S^{-1}\sum_{\mathbf{K}}$ in Eq. (28). Now the shift and width of the resonance frequency may be rewritten in the form

$$\Delta\Omega=\Omega-\Omega_0=-\frac{(\Omega_0)^{3/2}(\rho_l\eta)^{1/2}}{\pi(2\rho_s\mu)^{1/2}}\left\{1+\sqrt{2}\delta^{-1}S^{-1}\int\frac{d\mathbf{K}}{(2\pi)^2}|\xi(\mathbf{K})|^2K[a(K\delta)-\sqrt{2}/K\delta+\sqrt{2}\cos^2\phi]\right\}\ , \tag{24}$$

$$\Gamma=\frac{(\Omega_0)^{3/2}(\rho_l\eta)^{1/2}}{\pi(2\rho_s\mu)^{1/2}}\left\{1+\sqrt{2}\delta^{-1}S^{-1}\int\frac{d\mathbf{K}}{(2\pi)^2}|\xi(\mathbf{K})|^2K[\sqrt{2}/K\delta-b(K\delta)]\right\}. \tag{25}$$

In writing Eqs. (24) and (25) we introduce the following notations: $\Omega_0=(\pi/d)(\mu/\rho_s)^{1/2}$, which is the resonance frequency of a free quartz-crystal film, and

$$\delta=(2\eta/\Omega_0\rho_l)^{1/2}\ ,\quad a(t)=[(1+4t^{-4})^{1/2}+1]^{1/2}\ ,$$
$$b(t)=[(1+4t^{-4})^{1/2}-1]^{1/2}\ . \tag{26}$$

The first terms in braces in Eqs. (24) and (25) define the shift $\Delta\Omega_s$ and the broadening Γ_s of the shear resonance at the smooth crystal-liquid interface, respectively. The presence of surface roughness leads to the additional decrease $\Delta\Omega_{\mathrm{rh}}$ and broadening of the resonance frequency.

III. DISCUSSION

Equations (24) and (25) constitute the central result in the study of the influence of roughness on the resonance frequency ω_r. In this section we discuss the dependencies of the frequency shift on the viscosity and density of a fluid, and on correlation properties of roughness. Let us consider two types of surface morphologies.

A. Periodical corrugation, $\xi(\mathbf{R})=h\sin(2\pi y/l)$

In this case $\mathbf{K}=(0,2\pi n/l)$ and $\xi(\mathbf{K})=h(\delta_{n,1}-\delta_{n,-1})/2i$, where $n=0,\pm1,\pm2,\ldots$, and $\delta_{n,\pm1}$ is the Kronecker symbol. Then Eq. (24) transforms to

$$\Delta\Omega=-\frac{(\Omega_0)^{3/2}(\rho_l\eta)^{1/2}}{\pi(2\rho_s\mu)^{1/2}}\left\{1+\frac{h^2}{l^2}F(l/\delta)\right\}, \tag{27}$$

with

$$F(t)=\sqrt{2}\pi t[a(2\pi/t)-t/(\pi\sqrt{2})+\sqrt{2}\cos^2\phi] . \tag{28}$$

The scaling function $F(l/\delta)$ has the following asymptotic behavior:

$$F(l/\delta)=l/\delta\begin{cases}\pi^2\delta/l+2\pi\cos^2\phi & \text{at } l/\delta\gg1\\ 2\pi-l/\delta+2\pi\cos^2\phi & \text{at } l/\delta\ll1.\end{cases} \tag{29}$$

Equations (27)–(29) show that at an anisotropic surface the frequency shift depends on the direction of shear oscillations with respect to the symmetry axes of the surface.

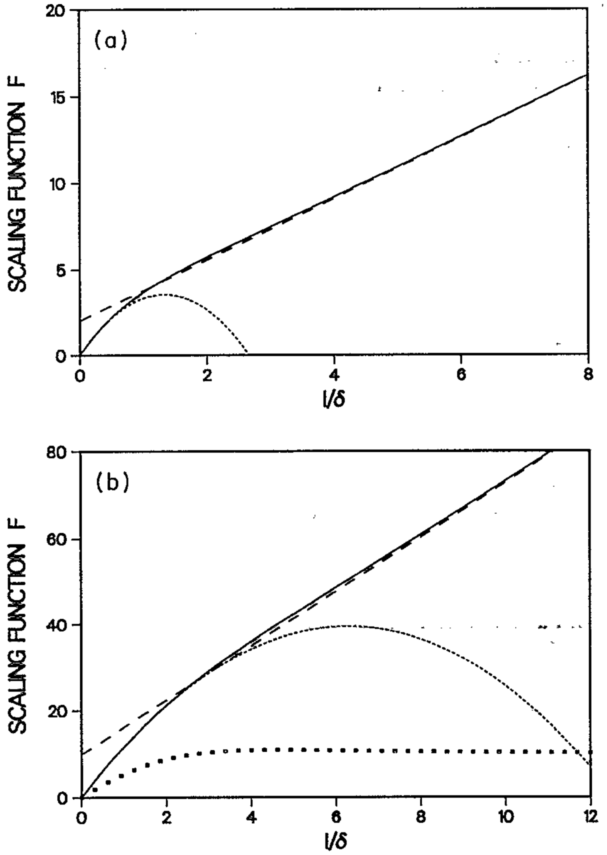

FIG. 1. Scaling functions for randomly rough (a) and periodical (b) surfaces. (a) The solid line is the result of exact calculations on the base of Eq. (30); dashed and dotted lines, respectively, are long- and short-range asymptotes (31) of the scaling function. (b) The solid line and squares are the results of exact calculations for the oscillations in the directions perpendicular and parallel to the grooves [$\cos\phi=1$ and $\cos\phi=0$, see Eq. (28)], respectively; dashed and dotted lines are long- and short-range asymptotes (29) for perpendicular oscillations.

B. Random roughness

It is often assumed that random roughness obeys the Gaussian distribution, which is characterized by two parameters: the rms height h and the correlation length along the surface, l. In this case $|\xi(\mathbf{K})|^2=\pi h^2l^2S\exp(-l^2K^2/4)$, and as before Eq. (24) for the frequency shift $\Delta\Omega$ may be rewritten in the form of Eq. (27), but with the different scaling function $F(l/\delta)$:

$$F(t)=\frac{t}{\sqrt{2}}\int dz\,z^2\exp(-z^2/4)\times[a(z/t)-\sqrt{2}t/z+1/\sqrt{2}] . \tag{30}$$

This function has the following asymptotic behavior:

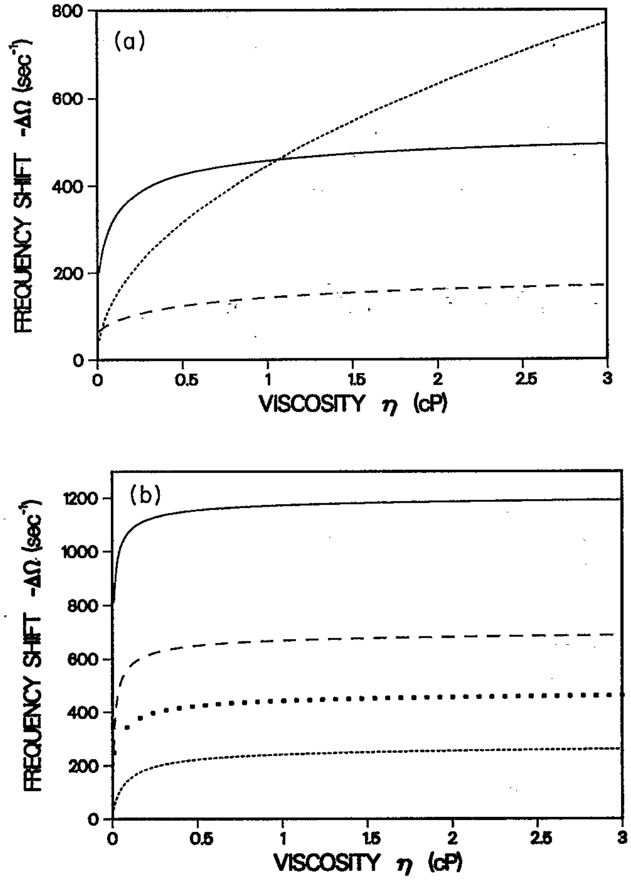

FIG. 2. Dependence of the resonance frequency shift on the viscosity of a liquid for randomly rough (a) and periodical (b) surfaces. (a) The solid and dashed lines are the roughness-induced shifts $-\Delta\Omega_{rh}$ for correlation lengths equal to $l=1000$ Å and 2500 Å, respectively; the liquid-induced shift $-\Delta\Omega_s\times10^{-1}$ for a smooth interface is shown by the dotted line. (b) The solid line and squares show the frequency shifts $-\Delta\Omega_{rh}$ for two values of corrugation periods $l=100$ and 250 nm in the case of oscillations in the direction perpendicular to the grooves; dashed and dotted lines give similar dependencies for the oscillations in the direction parallel to the grooves. The calculations were carried out for the following values of parameters: $\mu=2.947\times10^{11}\text{dyn}\,\text{cm}^{-2}$, $\rho_s=2.648\ \text{g}\,\text{cm}^{-3}$, $\Omega_0/2\pi=5$ MHz, $\rho_l=1\ \text{g}\,\text{cm}^{-3}$, and $h=30$ nm.

$$F(l/\delta)=l/\delta\begin{cases}\sqrt{\pi}+2\delta/l & \text{at } l/\delta\gg 1\\ 3\sqrt{\pi}-2l/\delta & \text{at } l/\delta\ll 1\ .\end{cases}\tag{31}$$

The results obtained show that the presence of roughness introduces a new length scale l that defines the rate of pressure decay as a function of the distance from the surface. The roughness-induced shift is proportional to the square of the "slope" of the roughness h/l, and to the one-parameter scaling function $F(l/\delta)$. The scaling parameter l/δ is the ratio of the correlation length (period) of the roughness to the decay length of fluid velocities. The behavior of the scaling function $F(l/\delta)$ over the whole range of the parameter l/δ for periodical and random surfaces is shown in Fig. 1.

Figure 2 presents the dependencies of the frequency shift on fluid viscosity. We see that the roughness leads to new viscosity dependencies which do not appear in the case of a smooth surface. The effect of roughness is most pronounced in the low viscosity limit, when the liquid-induced shift $\Delta\Omega_s$ at a smooth surface is small. The roughness-induced shift tends to a constant in the high viscosity limit when $\eta > l^2\Omega_0\rho_l/2$. These conclusions agree with experimental data[5] obtained for a rough solid surface in contact with methanol-water mixtures and alcohols.

Our calculations also demonstrate that the roughness-induced shift $\Delta\Omega_{rh}$ is mainly determined by the influence of fluid pressure on the oscillations of a quartz resonator. This effect is absent for a smooth interface. Figure 2(b) shows that in the case of shear oscillations along grooves of a periodical corrugation, where the pressure effect does not play any role, the shift $\Delta\Omega_{rh}$ is much smaller than for oscillations in the perpendicular direction. It should be stressed that the influence of weak surface roughness on the frequency shift cannot be explained in terms of the mass of liquid trapped by surface cavities, as was proposed in previous papers.[8,9]

Our results show that the QCM measurements in liquid can provide valuable information about the geometrical structure of the interface. To extract this information one must perform experiments for different values of viscosities, and obtain the relative shift $\Delta\Omega_{rh}/\Delta\Omega_s$ as a function of η. (The shift for a smooth interface, $\Delta\Omega_s$, can be calculated for given values of viscosity and density.) For the frequencies used in QCM, $\Omega_0/2\pi\approx 2-10$ MHz, the possible values of the decay length δ lie in the interval 10^2-10^4 nm. This means that if the correlation length of the roughness is of the order of 10^2-10^4 nm, then its value can be estimated by the QCM method comparing the viscosity dependence of the relative frequency shift with the calculated function $(h/l)^2F(l/\delta)$. For smaller or larger values of l only parameter h^2/l can be found from QCM data. The accuracy of determining the root-mean-square height of the roughness is limited by the accuracy of the QCM measurements (about 1 Hz). Equation (27) shows that for $l\approx 10^2$ nm the accuracy of determining h equals 5 nm.

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