Frequency shift of a quartz crystal oscillator bounded by a self-affine fractal rough surface in contact with a liquid

George Palasantzas
Physics Department, Northeastern University, Boston, Massachusetts 02115
(Received 16 December 1993)

An investigation of the coupling of shear oscillations of a quartz crystal resonator bounded by a self-affine rough surface with dumped waves in a liquid is performed. Calculation of the roughness effect is achieved in terms of a correlation model for self-affine fractal rough surfaces with analytic form of the associated roughness spectrum $G(k) \propto (1+ak^2\xi^2)^{-1-H}$.

PACS number(s): 68.45.−v, 68.15.+e, 68.35.Gy

There is a wide range of problems including surface wetting, film growth, phase transitions in absorbed films, characterization of surface processes in electrochemical systems, polymer solutions, etc., for which the topic of interfacial friction and viscoelasticity of thin surface layers [1–3], is of crucial importance. The quartz crystal microbalance (QCM) technic is a sensitive probe of interfacial friction and viscoelasticity [2,3]. The study of the frequency shift of the quartz resonance in contact with liquids has been investigated in a number of experimental works [4,5]. These studies inspired various theoretical attempts to describe the coupling of shear modes to liquid motion where a common feature was the neglection of surface microscopic characteristics [4,6,7]. However, it is an experimental fact that surface roughness can significantly affect the resonance frequency of the quartz oscillator [5,8]. Schumacher *et al.* [8] attributed the induced frequency shift due to surface roughness to additional mass of liquid trapped by surface cavities *(trapped liquid* model) and they concluded that variations in surface roughness during electrochemical oxidation has the most important contribution to the measured frequency shift. Beck *et al.* [8] made the assumption that surface roughness can increase energy dissipation into the liquid.

The basic scenario of interfacial liquid structure and roughness effect had already been presented by Yang *et al.* [5] but not in a completely developed frame. Very recently a treatment where microscopic properties of surface roughness were taken into account properly, was presented by Urbakh *et al.* [9]. They solve the problem of the coupling of shear oscillations of a quartz crystal bounded by a rough surface with damped waves in a liquid, by the method of Raleigh and Fano [9]. This procedure was applied on the linearized Navier-Stokes equations for a liquid in convolution with a harmonic equation to describe the elastic displacement of the crystal, as well as the balance between the crystal energy and that dissipated into the liquid. As the authors in Ref. [9] conclude, there is a relation between frequency shift and roughness spectrum or its associated fourier transform the height-height correlation function. They demonstrated by considering a periodically rough surface that the roughness induced frequency shift is mainly determined by the influence of fluid pressure on the oscillations of the quartz resonator *(fluid pressure* model) which as an effect is completely absent for a smooth surface. However, a more close examination of the fluid pressure model [9], and that of the trapped liquid model [8], is necessary for the case of random surfaces.

Up to now a quantitative analysis of the effects of surface roughness on the frequency shift has been performed for a special form of the roughness spectrum, $G(k) \propto \delta(\mathbf{k}-\mathbf{k}_\lambda)$ which corresponds to a wavy-sinusoidal surface of wavelength λ and demonstrates the effect of fluid pressure significantly due to orientational preference relative to the direction of oscillations, as well as for random Gaussian roughness with roughness spectrum $G(k) \propto \sigma^2 e^{-ak^2\xi^2}$ [9]. In the later case, the random surface is characterized by two degrees of freedom, namely, the rms surface width σ and an in-plane correlation length ξ. However, none of the previous cases corresponds to rough surfaces which are characterized with self-affine fractal scaling. In this case, the roughness spectrum posses a power law behavior over finite length scales where apart of the effect of σ and ξ, a third parameter enters the scenario which is the degree of surface irregularity. The latter is described by a roughness or "static" exponent $H, 0<H<1$ [10–14]. Therefore, an investigation of the effect of H on the frequency shift of the quartz resonator is in order. Apart from surface roughness characterization purposes, an examination is required of the impact of these models (fluid pressure, and trapped liquid) on a more general class of surface roughness as long as their predictions, relation, and correctness is concerned for real time applications which involve random surfaces.

Resonance frequency theories. For a quartz resonator with a flat boundary in contact with bulk liquid the frequency shift is given by [7] $\Delta\Omega_{\text{smooth}} = -\Omega_0^{3/2}(p_1 n)^{1/2}/\pi(2p_s\mu)^{1/2}$. The minus sign denotes decrease in frequency. The frequency shift due to the presence of surface roughness under the "fluid pressure" model [9], is given by

$$\Delta\Omega = -\frac{\Omega_0^{3/2}(p_1 n)^{1/2}}{\pi(2p_s\mu)^{1/2}}[1+f(\delta)] , \tag{1a}$$

$$f(\delta) = \frac{\sqrt{2}}{\delta}\int \frac{d^2\mathbf{k}}{(2\pi)^2} G(k)k[a(k\delta) - \sqrt{2}/k\delta + \sqrt{2}\cos^2\phi] . \tag{1b}$$

In Eq. (1b), the function $G(k)$ is related to the roughness spectrum. $\Omega_0=(\pi/d)(\mu/p_s)^{1/2}$ is the resonance frequency of the free quartz crystal with d the average thickness of the surface boundary, n is the liquid viscosity coefficient, p_s is the density of the quartz crystal, and μ is the shear modulus of the quartz crystal. ϕ is the angle between the two-dimensional vector $\mathbf{k}$ and the direction of oscillation of the quartz oscillator. The function $a(x)$ is defined by $a(x)=[(1+4x^{-4})^{1/2}+1]^{1/2}$, and $\delta=(2n/\Omega_0 p_1)^{1/2}$ is the decay length of the fluid velocity that is usually to the order of $0.1-1.0$ μm. Equations (1) were derived under the assumptions that $\delta \gg \sigma$, and $\xi \gg \sigma$ (small-slope limit) on which we shall limit our numerical calculations. The function $f(\delta)$ represents the roughness contribution on the frequency shift which is given by

$$\Delta\Omega_{\text{rough}}=-\frac{\Omega_0^{3/2}(p_1 n)^{1/2}}{\pi(2p_s\mu)^{1/2}}f(\delta) \ . \tag{2}$$

In terms of the trapped liquid model [8], the roughness induced frequency shift is given by

$$\Delta\Omega_{\text{rough}_t}=-\frac{\Omega_0^{3/2}(p_1 n)^{1/2}}{\pi(2p_s\mu)^{1/2}}f_t(\delta) \ , \quad f_t(\delta)=\frac{1}{\pi}\frac{\epsilon}{\delta} \ , \tag{3}$$

where ϵ is the mean thickness of trapped liquid. Comparing Eqs. (1b) and (3), we can define an effective mean thickness ϵ_f for the liquid trapped by surface cavities as $\epsilon_f=\pi\delta f(\delta)$. The later will be used for a quantitative comparison of previously mentioned models.

Roughness model. In nature, there is a wide variety of rough surfaces which are described in terms of self-affine fractal scaling, for example, the nanometer scale topology of vapor deposited metal films under nonequilibrium conditions [10]. The surface is defined by a vertical height profile above a horizontal xy plane, and is represented by a single valued random function $z(\mathbf{r})$ of the in-plane positional vector $\mathbf{r}=(x,y)$. The difference $z(\mathbf{r})-z(\mathbf{r}')$ is assumed to be a Gaussian random variable whose distribution depends on the relative coordinates $(x'-x,y'-y)$ such that $g(\mathbf{R})=\langle[z(\mathbf{r})-z(\mathbf{r}')]^2\rangle$, $\mathbf{R}=\mathbf{r}'-\mathbf{r}$. For an isotropic surface in x-y directions we may assume that $g(\mathbf{R})\propto R^{2H}$ with $0<H<1$. This kind of surface roughness can be attributed to self-affine fractal surfaces as defined by

Mandelbrot in terms of fractional Brownian motion [14]. The roughness exponent H determines the surface texture or the degree of surface irregularity, and is associated with a local fractal dimension $D=3-H$ [14,15]. For $R\to\infty$, $g(\mathbf{R})\to\infty$ and $g(R)/R^2\to 0$ (surface asymptotically flat) which is a rather ideal case since on real surfaces $g(R)$ at large length scales may saturate to the value $2\sigma^2$. This implies the existence of an effective roughness cutoff ξ (correlation length) such that for $R\ll\xi$; $g(R)\propto R^{2H}$, and for $R\gg\xi$; $g(R)\approx 2\sigma^2$ [11–13]. The parameter $\sigma=\langle z(\mathbf{0})^2\rangle^{1/2}$ is the rms saturated surface roughness. The height-height correlation $C(R)=\langle z(\mathbf{R})z(\mathbf{0})\rangle$ is related to $g(R)$ by $g(R)=2\sigma^2-2C(R)$. The effect of this kind of surface roughness can be studied in many cases quantitatively, since roughness enters through the surface height-height correlation function or its Fourier transform the roughness spectrum [11–13].

Roughness spectrum. We define the Fourier transform of $z(\mathbf{r})$ by $z(\mathbf{k})=(2\pi)^{-2}\int z(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d^2\mathbf{r}$, and the height-height correlation by $C(\mathbf{r})=A^{-1}\int\langle z(\mathbf{p})z(\mathbf{p}+\mathbf{r})\rangle d^2\mathbf{p}$ with A being the macroscopic surface area. The roughness spectrum is given by $\langle|z(\mathbf{k})|^2\rangle=A(2\pi)^6\int C(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d^2\mathbf{r}$. The function $G(k)$ is related to $\langle|z(\mathbf{k})|^2\rangle$ by $G(k)=(2\pi)^2/A\langle|z(\mathbf{k})|^2\rangle$, and is normalized such that $\int G(\mathbf{k})d^2\mathbf{k}=(2\pi)^2\sigma^2$ in accordance with the definitions followed by Urbakh *et al.* [9].

There is a specific class correlation functions for self-affine fractals, called *K correlations,* with analytic form of roughness spectrum [11]

$$\langle|z(\mathbf{k})|^2\rangle=\frac{A}{(2\pi)^5}\frac{\sigma^2\xi^2}{(1+ak^2\xi^2)^{1+H}} \ . \tag{4}$$

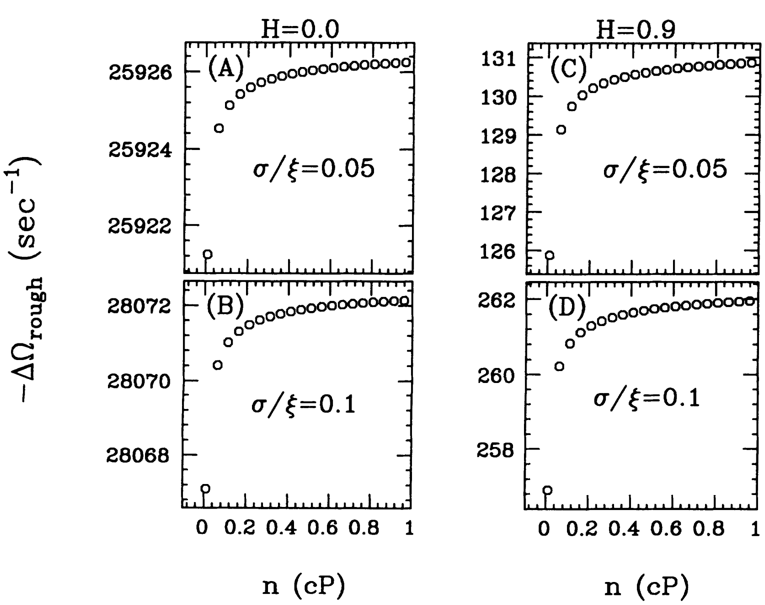

FIG. 1. Calculation of the frequency shift $-\Delta\Omega_{\text{rough}}$ for $\sigma=20.0$ nm as a function of the viscosity coefficient n (cP). (a) $\xi=400.0$ nm, $H=0.0$; (b) $\xi=200.0$ nm, $H=0.0$; (c) $\xi=400.0$ nm, $H=0.9$; (d) $\xi=200.0$ nm, $H=0.9$.

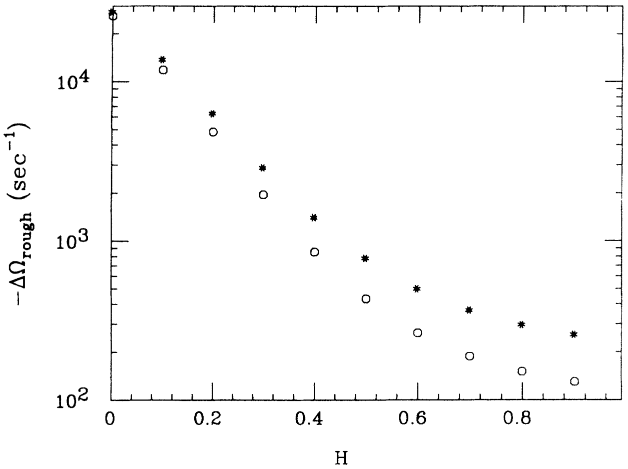

FIG. 2. Calculation of the frequency shift $-\Delta\Omega_{\mathrm{rough}}$ for $\sigma=20.0$ nm and $n=0.1$ cP as a function of the roughness exponent H. Circles: $\xi=400.0$ nm; stars: $\xi=200.0$ nm.

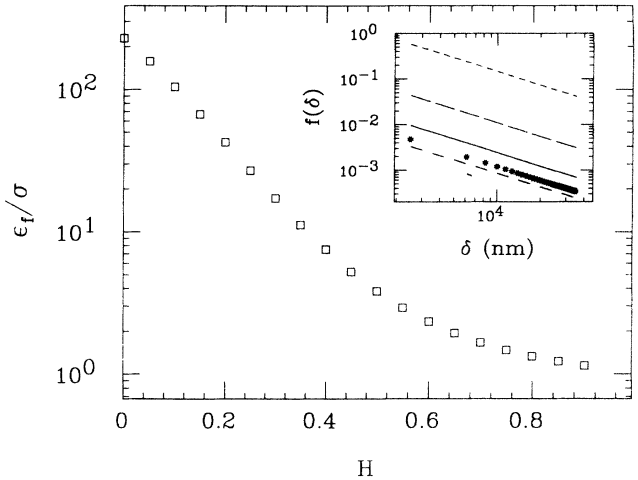

FIG. 3. Schematics of the calculated effective thickness ϵ_f in units of σ as a function of H for $\xi=400$ nm, $\sigma=20$ nm, and $n=0.1$ cP. The inset depicts calculations of $f(\delta)$ as a function of δ for $\sigma=20$ nm, $\xi=400$ nm and various values of H. Stars indicate calculations of $f_t(\delta)$ with $\epsilon=2\sigma$.

The parameter a is given by $a=(1/2H)[1-(1+a\pi^2\xi^2/a_0^2)^{-H}]$ with a_0 being the atomic spacing. In Eq. (1b) the natural regime of integration is $0\leq k\leq\pi/a_0$. In the limit $H\rightarrow 0$, Eq. (4) leads to correlations related to logarithmic roughness which are encountered in various roughening transition systems, [16,17], and the parameter a takes the form $a=\frac{1}{2}\ln[1+a\pi^2\xi^2/a_0^2]$.

Selected numerical results discussion. Since the effect of surface roughness is more pronounced for small values of the viscosity coefficient, we shall limit our study in the regime of values for n, $0.01\leq n\leq 1.0$ cP. The calculations were carried out for the parameter values: $\mu=2.947\times10^{11}$ dyn/cm^2, $p_s=2.648$ g/cm^3, $\Omega_0/2\pi=5$ MHz, $p_1=1.0$ g/cm^3, $a_0=0.27$ nm.

In order to gauge which parameter among H and σ/ξ has the most drastic effect on $\Delta\Omega_{\mathrm{rough}}$, we contrasted calculations in two rather "extreme" cases for H, namely, $H=0$ and $H=0.9$. As the comparison shows for $H=0.9$, reduction of the ratio σ/ξ by half can cause an enormous reduction of $\Delta\Omega_{\mathrm{rough}}$ even closely by half [see Figs. 1(c) and 1(d)]. In the opposite case for very jagged surfaces ($H\sim0$), $\Delta\Omega_{\mathrm{rough}}$ becomes less sensitive to changes of σ/ξ. This implies that for large H, the influence of the fluid pressure on the oscillations is mainly affected by the ratio σ/ξ. It should be also noted that $\Delta\Omega_{\mathrm{rough}}$ is not very sensitive to changes of the viscosity for $n>0.5$ cP. In fact, $\Delta\Omega_{\mathrm{rough}}$ tends to a constant value at high viscosities which is in agreement with experimental results [5], obtained on rough solid surfaces in contact with methanol-water mixtures and alcohols (see also Ref. [9]). In Fig. 2, we examine $\Delta\Omega_{\mathrm{rough}}$ as a function of H for fixed n, σ, and ξ. A strong dependence on H is observed for $0.0\leq H\leq 0.6$ which becomes more pronounced as the ratio σ/ξ is decreased.

Therefore, we can conclude that H has the dominant effect on $\Delta\Omega_{\mathrm{rough}}$ comparatively to σ/ξ.

This result can be significant for roughness studies in cases where the involved surface topology is highly irregular (in Ref. [12], $H=0.2$ and $\xi=700$ nm). In this case, for example, the applicability of scanning tunneling or atomic force microscopy suffers due to finite tip-curvature roundoff effects causing the surface to appear smoother (larger H) than it is in reality. On the other hand, QCM measurements with liquids can offer a suitable way to study the surface topology as is also described in detail by Urbakh *et al.* [9].

Model comparison. Since the surfaces we consider are isotropic random ones, there will be no dependence on the direction of the oscillations. For nanoscale roughness in the limits $\sigma\ll\xi$, $\sigma\ll\delta$, $\Delta\Omega_{\mathrm{rough}}\approx W(H)/\delta$ but with $W(H)$ increasing dramatically with decreasing H (inset, Fig. 3). For comparison purposes we calculated $\Delta\Omega_{\mathrm{rough}_t}$ with $\epsilon=2\sigma$. For pure Gaussian roughness $\sim e^{-ak^2}$ or $H\rightarrow 1$ (e.g., Fourier transform of the correlation $\sim e^{-(R/\xi)^{2H}}$) [11–13], it is expected that $\epsilon_f\approx\sigma$. This is because the surface possesses a smooth valley-hill topology with the cavity size responsible for liquid trapping (if we assume so) determined by σ. If $H<1$, the irregularity increases by introducing additional cavities (see Voss [18], for topological graphics). As a result, a larger mass of liquid can be trapped which will cause ϵ_f to become larger than σ. The dependence ϵ_f on H can be seen in Fig. 3. Therefore, for both models, fluid pressure and trapped liquid, for the case of isotropic random surfaces we observe similar qualitative behavior since there is no direction dependence of the surface oscillations that can discriminate between these two models as in the case of a sinusoidal surface. Furthermore, combination of these two theories can lead to a quantitative estimation of the mean liquid thickness ϵ_f [19].

In conclusion, in this report we correlated known information in order to study the effect of a more general class of surface roughness (self-affine fractal), on the frequency shift of a quartz crystal resonator in contact with bulk liquid. It was observed that the most prominent effect comes from the roughness or "static" exponent H which characterize the degree of surface irregularity. In addition, a quantitative comparison of two proposed models to describe the frequency shift due to surface roughness was performed, which led finally to an effective relationship between them.

It is my pleasure to acknowledge partial support from the NSF Grant No. DMR 9204022.

[1] *Fundamentals of Friction,* Vol. 220 of *NATO Advanced Study Institute Series B: Physics,* edited by I. L. Singer and H. M. Pollock (Kluwer, Dordrecht, 1992).

[2] E. T. Watts, J. Krim, and A. Widom, Phys. Rev. B **41**, 3466 (1990).

[3] D. Johannsmann, K. Mathauer, G. Wegner, and W. Knoll, Phys. Rev. B **46**, 7808 (1992).

[4] K. K. Kanazawa and J. G. Gordon II, Anal. Chim. Acta **175**, 99 (1985).

[5] M. Yang, M. Thompson, and W. C. Duncan-Hewitt, Langmuir **9**, 802 (1993).

[6] S. Bruckenstein and M. Shay, Electrochim. Acta **30**, 1295 (1985).

[7] C. E. Reed, K. K. Kanazawa, and J. H. Kaufman, J. Appl. Phys. **68**, 1993 (1990).

[8] R. Schumacher *et al.*, Surf. Sci. **163**, L621 (1985); R. Schumacher *et al.*, J. Electroanal. Chem. **216**, 127 (1987); R. Beck *et al.*, Phys. Chem. **92**, 1363 (1988); R. Beck *et al.*, J. Electrochem. Soc. **139**, 453 (1992).

[9] M. Urbakh and L. Daikhin, Phys. Rev. B **49**, 4866 (1994); Lord Rayleigh, Philos. Mag. **14**, 70 (1907); *Theory of Sound,* 2nd ed. (Dover, New York, 1945), Vol. II, p. 89; U Fano, J. Opt. Soc. Am. **31**, 213 (1941).

[10] *Dynamics of Fractal Surfaces,* edited by F. Family and T. Viscek (World Scientific, Singapore, 1991).

[11] G. Palasantzas, Phys. Rev. B **48**, 14 472 (1993); **49**, 5785 (E) (1994); Phys. Rev. E **49**, 1740 (1994).

[12] S. K. Sinha, E. B. Sirota, S. Garoff, and H. B. Stanley, Phys. Rev. B **38**, 2297 (1988).

[13] R. Pynn, Phys. Rev. B **45**, 602 (1992); W. Weber *et al.*, *ibid.* **46**, 7953 (1992); G. Palasantzas *et al.*, *ibid.* **48**, 2873 (1993).

[14] B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, New York, 1982).

[15] S. Alexander, in *Transport and Relaxation in Random Materials,* edited by J. Klafter, R. Rubin, and M. F. Schlesinger (World Scientific, Singapore, 1987).

[16] J. G. Amar and F. Family, Phys. Rev. Lett. **64**, 542 (1990); J. Krug *et al.*, *ibid.* **64**, 2332 (1990); J. M. Kim *et al.*, *ibid.* **64**, 2333 (1990); D. A. Huse *et al.*, Phys. Rev. B **41**, 7075 (1990); D. A. Huse *et al.*, Phys. Rev. A **41**, 7075 (1990); T. Hwa *et al.*, Phys. Rev. Lett. **66**, 441 (1990); B. M. Forrest *et al.*, *ibid.* **64**, 1405 (1990).

[17] $\lim_{H\to 0} 1/H[x^H - 1] \to \ln(x)$.

[18] R. F. Voss, in *Fundamental Algorithms for Computer Graphics,* edited by R. A. Earnshaw (Springer-Verlag, Berlin, 1985), p. 808; R. F. Voss, in *Scaling Phenomena in Disordered Systems,* edited by R. Pynn and A. Skjeltorp (Plenum, New York, 1985), p. 1.

[19] For a detailed comaprison of experimental data with the trapped liquid model see also, K. K. Kanazawa and J. Gordon, J. Electrochem. Soc. **93**, 2788 (1993).