

SUPPORTING INFORMATION

ANOMALOUS BEHAVIOR OF ULTRA-LOW-AMPLITUDE CAPILLARY WAVES. A GLIMPSE OF THE VISCOELASTIC PROPERTIES OF INTERFACIAL WATER?

Antonio Raudino^{a*}, Domenica Raciti^a, Mario Corti^{b,c}.

^a *Department of Chemical Sciences, University of Catania, Viale A. Doria 6-95125, Catania, Italy*

^b *CNR-IPCF Viale F. Stagno d'Alcontres, 37, 98158 Messina, Italy*

^c *LITA, University of Milano, Via Fratelli Cervi 93, 20090 Segrate Milano, Italy*

A) EQUATION OF MOTION FOR AN OSCILLATING DROP (OR BUBBLE).

Following Brenn (Brenn, G. *Analytical Solutions for Transport Processes*; Springer: New York, 2016), the equation of motion stemming from the Navier-Stokes equation (8) of the main text reads:

$$\frac{\partial}{\partial t}(E_s^2 \psi_s) = \nu E_s^4 \psi_s \quad (1A)$$

where $\nu \equiv \eta/\rho$ is the kinematic viscosity. In spherical polar coordinates the axisymmetric E_s^2 operator reads:

$$E_s^2 \equiv \frac{\partial^2}{\partial r^2} + \frac{\sin\theta}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \right) \quad (2A)$$

and $E_s^4 = E_s^2 E_s^2$. The *stream function* ψ_s is related to the fluid velocity components by the relationships:

$$v_r = -\frac{1}{r^2 \sin\theta} \frac{\partial \psi_s}{\partial \theta} \quad v_\theta = \frac{1}{r \sin\theta} \frac{\partial \psi_s}{\partial r} \quad (3A)$$

Solution to eq.(1A) can be expressed as a function of the displacement of the bubble (drop) deformation from the equilibrium spherical shape $\ell(\theta, t) = \sum_n \ell_n(t) P_n(\theta)$ through the boundary condition (11) of the main text: $v_r|_s = v_r'|_s \approx \frac{\partial \ell(\theta, \phi, t)}{\partial t}$. Combining these latter equations with eqs.(1A)-(3A) we found a linear relationship between the surface velocity of the fluid and the deformation of the bubble (drop). Solving the resulting partial differential equation by the method of separation of variables, we get an ordinary differential equation for the time-dependent part:

$$\frac{d\ell_n(t)}{dt} + \alpha_n \ell_n(t) = 0 \quad (4A)$$

The still unknown complex coefficients α_n appearing in the above linear differential equation can be calculated by applying the proper boundary conditions. These are given by eqs.(14a,b) of the main text. After some algebra they lead to a transcendental equation as reported by eq.(15). It can be easily seen that generally α_n is a complex quantity (purely imaginary in the zero-viscosity limit and real at very high viscosities). Equation (4A) with complex-valued α_n coefficients is equivalent to eq.(12) of the main text, provided the normal frequency ω_n^0 and the damping coefficient γ_n are both real numbers related to the real and imaginary part of α_n through eq.(13).

The main advantages of the notation reported by eq.(15) of the main text are twofold: a) all the quantities contained in eq.(15) are real numbers; b) the restoring force and the damping effects appear explicitly, enabling us to systematically improve the equation of motion of the oscillating interface, as we did through eqs.(23) and (24).

B) ASYMPTOTIC EQUATIONS FOR CALCULATING THE COMPLEX FREQUENCIES OF AN OSCILLATING DROP (BUBBLE).

Here we report two relevant asymptotic formulas for the calculation of the frequencies and dissipation of oscillating drops and bubbles. The starting point is the non-linear equation (15) of the main text. In the high viscosity limit ($qR \rightarrow 0$) the term $Q_n(qR)$ of eq.(15) takes the simple form: $Q_n(qR) \approx \frac{q^2 R^2}{2n+3} + O(q^4 R^4)$. Inserting this result into eq.(15) and expanding the resulting expression in power series of $qR \equiv q(\alpha_n)R$, we get a cubic equation in α_n :

$$\frac{\alpha_{n,0}^2}{\alpha_n^2} \approx W_n - K_n \frac{1}{\alpha_n} \frac{1-\lambda_2\alpha_n}{1-\lambda_1\alpha_n} + O(\alpha_n) \quad (1B)$$

Where we set: $W_n \equiv \frac{n\rho}{n\rho+(n-1)\rho} \frac{n(n+2)^2}{2n+1} - 1$ and: $K_n \equiv \frac{n\rho}{n\rho+(n-1)\rho} 2(n-1)(n+1)(n+2) \frac{\eta}{\rho R^2}$.

Perturbation solution to eq.(1B) yields the two results given by eqs.(19a) and (19b) of the main text.

Analogously, in the opposite low-viscosity limit ($qR \rightarrow \infty$) we get: $Q_n(qR) \approx -iqR + O(q^{-1}R^{-1})$. Inserting this result into eq.(15) and expanding the resulting expression in power series of $q(\alpha_n)R$ we obtain to the leading terms:

$$\frac{\alpha_{n,0}^2}{\alpha_n^2} \approx G_n \frac{1}{\alpha_n} \frac{1-\lambda_2\alpha_n}{1-\lambda_1\alpha_n} - 1 + O(i\alpha_n^{-3/2}) \quad (2B)$$

where $G_n \equiv \frac{n\rho}{n\rho+(n-1)\rho} 2(2n+1)(n+2) \frac{\eta}{\rho R^2}$. Perturbation solution to eq.(2B) yields eqs.(20a,b) of the main text.

C) NON-LINEAR DIFFERENTIAL EQUATION WITH AMPLITUDE-DEPENDING FRICTION.

Here we derive the constitutive eqs.(25a,b) which describe the non-linear relationship between the squared oscillator amplitude $L \ll A_n A_n^* >^{1/2}$ and the intensity B of the applied field. We start from the inhomogeneous differential equation (22) and substitute the friction coefficient γ_n by its analytical expression given by eqs.(24a,b). A particular solution to eq.(22) is: $\ell_n = A_n e^{i\alpha t}$, $\ell_n^* = A_n^* e^{-i\alpha t}$. Inserting this result into eq.(22) we obtain:

$$((\omega_n^o)^2 - \omega_n^2)A_n + i\omega\gamma_n(A_n, A_n^*)A_n = B \quad (1Ca)$$

$$((\omega_n^o)^2 - \omega_n^2)A_n^* - i\omega\gamma_n(A_n, A_n^*)A_n^* = B^* \quad (1Cb)$$

where $\gamma_n(A_n, A_n^*)$ is given by eq.(24) of the main text: $\gamma_n(A_n, A_n^*) \approx \frac{\gamma_n^{MIN}}{1 - \frac{\gamma_n^{MAX} - \gamma_n^{MIN}}{\gamma_n^{MAX}} \frac{|A_n A_n^*|}{A_{crit}^2}}$ when

$A_n < A_{crit}$ and $\gamma_n(A_n, A_n^*) = \gamma_n^{MAX}$ when $A_n > A_{crit}$. Notice that non-linear term in $A_n \cdot A_n^*$ arises from the relationship between γ_n and A_n assumed to hold in our amplitude-related friction model.

In the limit $\frac{\gamma_n^{MAX} - \gamma_n^{MIN}}{\gamma_n^{MAX}} \ll 1$ (i.e., small variation of the friction coefficient γ_n with viscoelasticity), we may easily solve the coupled non-linear algebraic equations (1Ca,b) by a standard perturbation procedure. Separating the real and imaginary parts of A_n we found that: $\langle A_n A_n^* \rangle^{\frac{1}{2}} = \langle A_n^2 \rangle^{\frac{1}{2}}$, as it should be. Neglecting higher order terms in the small dimensionless quantity $\frac{\gamma_n^{MAX} - \gamma_n^{MIN}}{\gamma_n^{MAX}}$, eventually we recover eqs.(25a,b).