Acid Polishing of Lead Crystal Glass

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0.1   Introduction

The industrial partner manufactures high quality lead crystal glassware. The cutting of decorative features in the glass damages the surface and the cuts are optically opaque; to restore transparency, the glass is polished in a solution of hydrofluoric (HF) and sulphuric acid (H_2SO_4.) The polishing process comprises three stages:

1. immersion in a polishing tank containing acid;

2. rinsing in a tank containing water; and

3. settlement of the solid reaction products in a settlement tank.

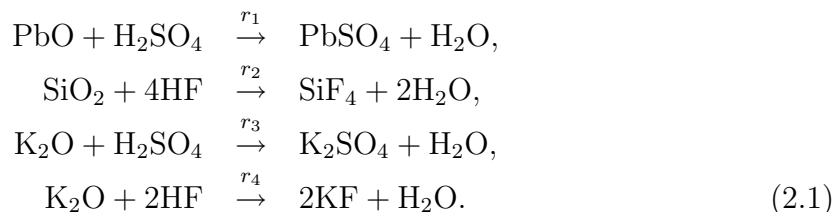   The manufacturer hopes to optimise its polishing process to

- minimise the health/environmental impact of the process;

- maximise throughput;

- maintain the sharpness of the cut edges while still polishing to an acceptable level of transparency.

   The study group was asked to focus on modelling three aspects of the process:

- the chemical reactions involved in the etching at the glass-acid solution interface;

- the removal of reaction products in the settlement tank.

- flow within the polishing tank;

0.2   Etching

The polishing process involves the dissolution of cut glass surfaces in a reservoir of hydrofluoric acid (HF) and sulphuric acid (H_2SO_4).[1] Lead crystal consists largely of lead oxide PbO, potassium oxide K_2O, and silica SiO_2, and these react with the acids according to the reactions

$$
\begin{aligned}
PbO + H_2SO_4 &\xrightarrow{r_1} PbSO_4 + H_2O, \\
SiO_2 + 4HF &\xrightarrow{r_2} SiF_4 + 2H_2O, \\
K_2O + H_2SO_4 &\xrightarrow{r_3} K_2SO_4 + H_2O, \\
K_2O + 2HF &\xrightarrow{r_4} 2KF + H_2O.
\end{aligned} \tag{2.1}
$$

The potassium salts and the silicon hexafluoride are soluble, but not the lead sulphate, which precipitates on the cut surface before being washed away in the rinsing bath. This rinsing action must have a chemical effect, with the water acting to dissolve the bonds which tie the sulphate crystals to the surface.

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[1]Thanks to J.J. Leahy of the Department of Chemical and Life Sciences (UL) who explained some chemistry to us.

0.2.1 Surface evolution

In general, if a surface is given by $F(\mathbf{x}, t) = 0$, then its velocity $\mathbf{v}$ satisfies $F_t + \mathbf{v}.\boldsymbol{\nabla}F = 0$, whence also $F_t + v_n|\boldsymbol{\nabla}F| = 0$, where $v_n = \mathbf{v}.\mathbf{n}$ denotes the normal velocity of the surface, and $\mathbf{n} = \dfrac{\boldsymbol{\nabla}F}{|\boldsymbol{\nabla}F|}$ is the unit normal. For example, if the surface is denoted by $z = s(x, y, t)$, then (taking $F = s - z$)

$$s_t = -\left[1 + |\boldsymbol{\nabla}s|^2\right]^{1/2} v_n, \tag{2.2}$$

where v_n is the normal downward removal rate of the surface. In general, we expect the reaction rates to increase with the curvature of the surface. Specifically, the mean curvature of the surface κ is defined by

$$2\kappa = \boldsymbol{\nabla}.\mathbf{n} = -\boldsymbol{\nabla}.\left[\frac{\boldsymbol{\nabla}s}{(1 + |\boldsymbol{\nabla}s|^2)^{1/2}}\right], \tag{2.3}$$

and thus

$$s_t = -\left[1 + |\boldsymbol{\nabla}s|^2\right]^{1/2} v_n \left\{\frac{\boldsymbol{\nabla}s}{(1 + |\boldsymbol{\nabla}s|^2)^{1/2}}\right\}, \tag{2.4}$$

and v_n is an decreasing function of its argument; hence (2.4) is a non-linear diffusion equation for s. As such, the surface will smooth as it is etched, thus explaining simply enough why polishing works.

0.2.2 Etching rate

We now wish to relate the etching rate v_n to the reaction rates of (2.1). We denote the reaction rates of the four reactions in (2.1) as r_1, r_2, r_3 and r_4, respectively, with units of moles per unit area per unit time. Denote further the densities of lead sulphate, silica and potassium oxide by ρ_P, ρ_S and ρ_K, respectively, their volume fractions within the crystal by ϕ_P, ϕ_S and ϕ_K, and their molecular weights by M_P, M_S and M_K. Then the density of species i in the crystal is $\phi_i\rho_i$, and its molar density is $\dfrac{\phi_i\rho_i}{M_i}$. Therefore if v_n is the rate of removal of the surface, then the rate of removal of species i from the surface is $\dfrac{\phi_i\rho_i v_n}{M_i}$, and this must be equal to the rate of reaction, thus

$$\frac{\phi_i\rho_i v_n}{M_i} = R_i. \tag{2.5}$$

In terms of the reaction rates r_j, we would have

$$R_P = r_1, \quad R_S = r_2, \quad R_K = r_3 + r_4. \tag{2.6}$$

The quantity

$$m_j = \frac{\phi_j\rho_j}{M_j} \tag{2.7}$$

is the molar density of species j, and if we denote

$$m = \sum_j m_j \tag{2.8}$$

as the molar density of the glass, then

$$f_j = \frac{m_j}{m} \tag{2.9}$$

is the fraction of sites in the crystal occupied by species j. It is natural to take

$$R_i = f_i F_i, \tag{2.10}$$

where F_i is the effective flux of external (acid) reactant to the surface, and thus (2.5) and (2.10) imply

$$mv_n = F_i. \tag{2.11}$$

It was observed that if one of the acids is not present, etching will not occur. For example, one can store sulphuric acid in a glass jar without damage; the hydrofluoric acid is also necessary to cause etching. And yet, the sulphuric acid must attack the lead sulphate. The mathematical part of this conundrum lies in the general impossibility of satisfying (2.11) for each species, since it would require the specific effective reaction rates F_i to be related to each other, and this is unrealistic. In order to determine what the etching rate v_n is, we thus need to consider in greater detail just what the surface reaction process is.

Physically, we can explain this conundrum in the presence of a single acid, say H_2SO_4, by means of the following conceptual picture. Imagine the glass as a crystal lattice — which it is not . but the concept is valid — where lead, silicon and potassium atoms are distributed at random. The sulphuric acid can pick off the lead atoms, and we suppose that it can excavate downwards into the lattice until it encounters a silicon atom. At this point, no further stripping is possible, and reaction at that horizontal location ceases. This stripping will happen at each point of the surface, and, supposing only vertical excavation is possible, eventually a molecularly rough surface will be obtained, in which only silicon atoms are exposed, thus preventing any further reaction.

In order to describe the surface reaction, we need to account for the molecularly rough surface, and to do this, we again suppose that the molecules are arranged in a lattice, with the horizontal layers denoted by an index i, with $i = 0$ indicating the initial surface, and i increasing with depth into the lattice. As etching proceeds, the surface will have exposed sites at different levels. We let ψ_i^j denote the fraction of exposed surface at level i of species j. As before, the specific effective reaction rate of species j is denoted F_j, and the species is present in a fraction of sites f_j in the crystal. Thus

$$\sum_j f_j = 1. \tag{2.12}$$

We define

$$\psi_i = \sum_j \psi_i^j \tag{2.13}$$

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to be the fraction of exposed sites at level i, and thus

$$\sum_{i=0}^{\infty} \psi_i = 1. \tag{2.14}$$

The reaction equations describe the evolution of exposed sites, and are

$$\dot{\psi}_i^j = -A_j \psi_i^j + f_j \sum_k A_k \psi_{i-1}^k, \quad i \geq 1,$$

$$\dot{\psi}_0^j = -A_j \psi_0^j. \tag{2.15}$$

The negative term in (2.15) represents the reactive rate of removal of exposed j sites, while the positive term represents the creation of new exposed sites (a fraction f_j of which are j sites). The quantities A_j (units s^{-1}) are given by

$$A_j = N F_j (\Delta x)^2, \tag{2.16}$$

where N is Avogadro's number (6×10^{23} mole^{-1}), and Δx is the lattice spacing (m). Note that the molar density is

$$m = \frac{1}{N(\Delta x)^3}, \tag{2.17}$$

so that (2.16) is

$$A_j = \frac{F_j}{m \Delta x}. \tag{2.18}$$

Thus the paradox (2.11) can be written as

$$v_n = A_j \Delta x, \tag{2.19}$$

and is a paradox unless the A_j's are equal.

Ideally, the solution for the total exposed site fraction ψ_i would tend to a Gaussian shaped travelling wave, whose speed would then be the effective etching rate, v_n. In practice, numerical solution of these equations indicates a travelling wave which also diffuses as it propagates (see figures 1 and 2.)

The computations also indicate that the solution varies smoothly with i, and this suggests examining the continuum limit of (2.15). To do this, we put

$$x = i\Delta x, \quad \psi^j(x, t) = \psi_i^j; \tag{2.20}$$

Taylor expanding about x, (2.15) becomes

$$\frac{\partial \psi^j}{\partial t} = -A_j \psi^j + f_j \sum_k A_k \left\{ \psi^k - \Delta x \frac{\partial \psi^k}{\partial x} + \frac{(\Delta x)^2}{2} \frac{\partial^2 \psi^k}{\partial x^2} \cdots \right\}, \tag{2.21}$$

with boundary condition

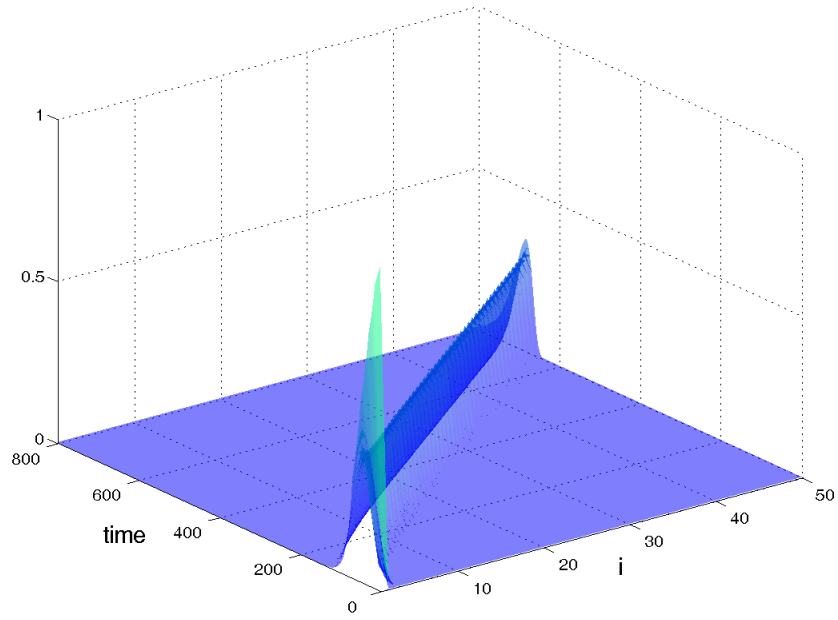$$\frac{\partial \psi^j}{\partial t} = -A_j \psi^j \quad \text{at} \quad x = 0. \tag{2.22}$$

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Figure 1: Development of $\phi = \phi_1 + \phi_2$ with $r_1 = 1$, $r_2 = 0.1$, $f_1 = 0.1$, $f_2 = 0.9$
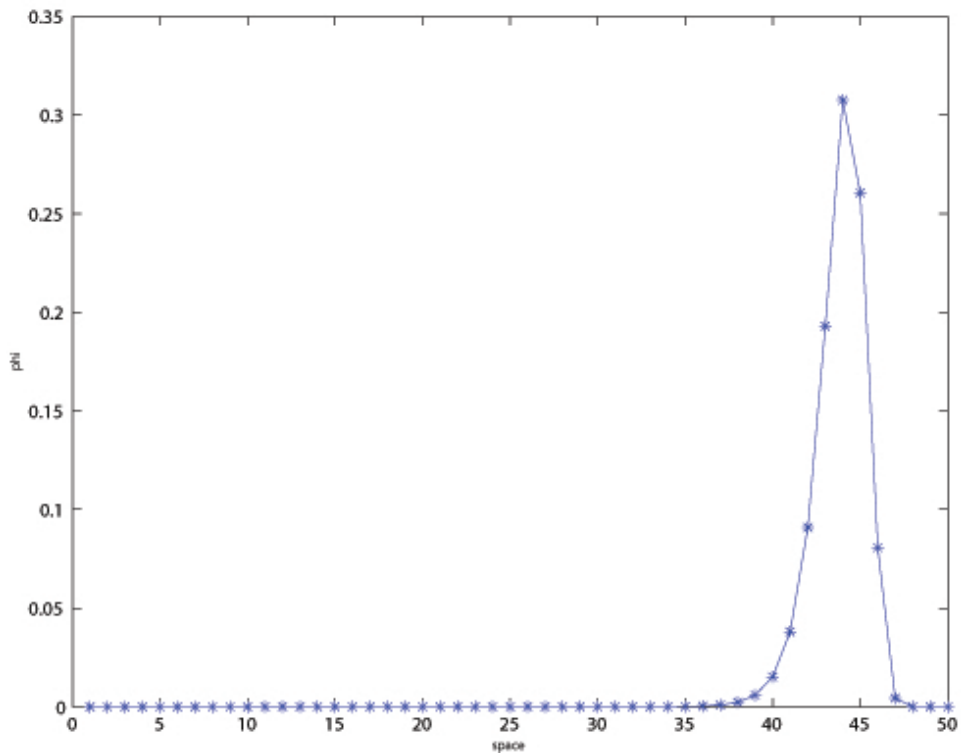

Figure 2: $\phi = \phi_1 + \phi_2$ at fixed t with $r_1 = 1$, $r_2 = 0.1$, $f_1 = 0.1$, $f_2 = 0.9$

The initial condition is

$$
\begin{aligned}
\psi^j &= 0 \quad \text{on} \quad t = 0, \; x > 0, \\
\psi^j &= f_j \quad \text{on} \quad t = 0, \; x = 0,
\end{aligned}
\tag{2.23}
$$

and the small diffusion terms induce an extra boundary condition (culled from the initial condition)

$$
\psi^j \to 0 \quad \text{as} \quad x \to \infty.
\tag{2.24}
$$

Summing (2.22) over j, we find that

$$
\frac{\partial \psi}{\partial t} + \sum_k v_k \frac{\partial \psi^k}{\partial x} = \sum_k D_k \frac{\partial^2 \psi^k}{\partial x^2},
\tag{2.25}
$$

where

$$
v_k = A_k \Delta x, \quad D_k = \tfrac{1}{2} v_k \Delta x,
\tag{2.26}
$$

and

$$
\psi = \sum_j \psi^j.
\tag{2.27}
$$

We see that if the A_k's are all equal, say to A, then the apparent paradox disappears, and the wave speed is $v_n = A\Delta x$, as suggested by (2.19). In addition there is a set of small diffusion coefficients D_k. We can see that these are small, since over the time l/v_n during which the front advances a distance l into the solid, the diffusion acts over a distance $\sqrt{Dl/v_n} \sim \sqrt{l\Delta x}$. This indicates that the surface is molecularly rough over the distance $\sqrt{l\Delta x}$.

Now let us consider what happens if the A_k's are unequal. We write (2.21) in the form

$$
\frac{\partial \psi^j}{\partial t} + f_j \sum_k v_k \frac{\partial \psi^k}{\partial x} = -A_j \psi^j + f_j \sum_k A_k \psi^k + f_j \sum_k D_k \frac{\partial^2 \psi^k}{\partial x^2},
\tag{2.28}
$$

with

$$
\psi^j = f_j \exp(-A_j t) \quad \text{at} \quad x = 0.
\tag{2.29}
$$

At this point it is convenient to scale the equation. We order the k's so that $v_1 = \min v_k$, and we then scale x and t as

$$
x \sim l, \quad t \sim \frac{l}{v_1},
\tag{2.30}
$$

and we define

$$
\varepsilon = \frac{\Delta x}{l}, \quad V_k = \frac{v_k}{v_1},
\tag{2.31}
$$

and note that $V_1 = 1$, $V_k > 1$ for $k > 1$. The dimensionless form of the equation is then

$$
\frac{\partial \psi^j}{\partial t} + f_j \sum_k V_k \frac{\partial \psi^k}{\partial x} = -\frac{1}{\varepsilon}\left[-V_j \psi^j + f_j \sum_k V_k \psi^k \right] + \varepsilon f_j \sum_k \tfrac{1}{2} V_k \frac{\partial^2 \psi^k}{\partial x^2},
\tag{2.32}
$$

with

$$\psi^j = f_j \exp\left(-\frac{V_j t}{\varepsilon}\right) \quad \text{at} \quad x = 0. \tag{2.33}$$

If we define the matrices B and V by

$$B_{jk} = f_j V_k, \quad V = \operatorname{diag} V_k, \tag{2.34}$$

then (2.32) is written succinctly as the linear equation

$$\boldsymbol{\psi}_t + B\boldsymbol{\psi}_x = \frac{1}{\varepsilon}\left[-V\boldsymbol{\psi} + B\boldsymbol{\psi}\right] + \tfrac{1}{2}\varepsilon B\boldsymbol{\psi}_{xx}, \tag{2.35}$$

where $\boldsymbol{\psi} = (\psi^1, \ldots, \psi^n)^T$, if there are n components.

We may conjecture what the solution of (2.35) should be. Physically, the quantities v_k in (2.26) represent the rate of etching of a surface of pure species k. Insofar as it is necessary to remove all species, it seems natural to suppose that the actual rate of etching will be $v_n = \min v_k = v_1$. In dimensionless terms, this suggests that the solution of (2.35) should (rapidly) tend to a solution in which $\boldsymbol{\psi}$ is non-zero, away from $x = st$, where we expect $s = \min V_k = V_1 = 1$ by choice of the scale for v_k. Inspecting (2.35), this suggests that we write[2]

$$x - st = \varepsilon\xi, \quad t = \varepsilon\tau, \tag{2.36}$$

and then (2.35) becomes

$$\boldsymbol{\psi}_\tau + (B - sI)\boldsymbol{\psi}_\xi = (B - V)\boldsymbol{\psi} + \tfrac{1}{2}B\boldsymbol{\psi}_{\xi\xi}, \tag{2.37}$$

with the appropriate boundary conditions being that

$$\boldsymbol{\psi} \to 0 \quad \text{as} \quad \xi \to \pm\infty. \tag{2.38}$$

The solution is constrained to be non-zero because of the normalising constraint (2.14), which in the present terms can be approximated as

$$\sum_j \int_{-\infty}^{\infty} \psi^j \, d\xi = 1. \tag{2.39}$$

The hyperbolic, diffusionless part of (2.35) has characteristic speeds λ, these being the eigenvalues of B. What happens along these characteristics is opaque, because of the linear source term. If we examine the diffusionless version of (2.37), we can see that there are steady exponential solutions $\boldsymbol{\psi} = \mathbf{c}e^{\alpha\xi}$, $\xi < 0$, $\boldsymbol{\psi} = 0$, $\xi > 0$, providing

$$\alpha(B - sI)\mathbf{c} = (B - V)\mathbf{c}, \tag{2.40}$$

---

[2]It should be noted that the continuum approximation really loses justification on the ξ scale, in which the lattice spacings are $\Delta\xi = 1$. However, for a glass, we can reclaim its justification, since random molecular spacings will yield a continuous variation with ξ when varied horizontally over the surface.

which is some kind of eigenvalue problem for α, given s (or vice versa). Normalisation of $\mathbf{c}$ follows from (2.29).

The question arises, how should both α and s be chosen? We apparently need $\alpha > 0$, and we would like for any solution where $s > V_1$ (if this is the actual wave speed) to have $\alpha < 0$, which (with $\boldsymbol{\psi} \to 0$ at $-\infty$) would then imply $\boldsymbol{\psi} \equiv 0$. In addition, we must have $c_i \geq 0$ for each i. These constraints appear mutually contradictory, and it remains to be seen what the structure of the solutions of (2.35) or (2.37) (with or without the diffusion term) actually is.

The industrial partner has agreed to supply samples of glass at various stages of the etching process; it is planned to produce scanning electron micrographs of each sample to validate the proposed model.

0.3 Settlement

For a sediment of uniform size, we define the volume fraction to be ϕ. Then mass conservation of the sediment takes the form

$$\phi_t + (\phi v)_z = 0, \tag{3.1}$$

where v is the average sediment velocity. Mass conservation of the liquid takes the form

$$-\phi_t + [(1-\phi)u]_z = 0, \tag{3.2}$$

where u is the fluid velocity. Adding these, we obtain the total flux condition

$$\phi v + (1-\phi)u = 0. \tag{3.3}$$

Additionally, we suppose that settling occurs at a rate

$$v - u = -v_s(\phi), \tag{3.4}$$

where v_s is the settling velocity. Typical assumptions are

$$v_s = v_0(1-\phi)^\nu, \tag{3.5}$$

where v_0 is the Stokes settling velocity,

$$v_0 = \frac{2}{9}\frac{\rho g a^2}{\mu}, \tag{3.6}$$

where μ is the viscosity, g is gravity, and a is particle radius.

From these it follows that $u = \phi v_s(\phi)$, and writing $z = -Z$, so that Z points downwards, we find

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial Z}[\phi(1-\phi)v_s(\phi)] = 0. \tag{3.7}$$

The particle flux is thus

$$q(\phi) = \phi(1-\phi)v_s(\phi), \tag{3.8}$$

and is a unimodal (one-humped) function of ϕ. The characteristic speed is thus

$$V(\phi) = q'(\phi), \tag{3.9}$$

and is a monotonically decreasing function of ϕ.

It is straightforward to solve (3.7), for example from an initially uniform concentration ϕ_0. The solution then consists of two uniform regions in which $\phi = 0$ and $\phi = \phi_0$, separated by a shock at $Z = V_s t$, where the uniform shock speed is given by

$$V_s = \frac{[q]}{[\phi]} = \{(1 - \phi)v_s\}|_{\phi_0}. \tag{3.10}$$

0.3.1 Variable grain size

Now suppose that the particulate has a grain size distribution $f(a; z, t)$, where a is particle radius; thus the volume fraction of particles is

$$\phi = \int_0^\infty f \, da, \tag{3.11}$$

and f has units of inverse length. Conservation of particle mass now takes the form

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial z}(fv) = 0, \tag{3.12}$$

where we also define the drift velocity

$$v - u = -v_s, \tag{3.13}$$

where u is the liquid velocity and, for example,

$$v_s(a, \phi) = v_0(a)(1 - \phi)^\nu. \tag{3.14}$$

Again we might take v_0 to be the Stokes settling velocity in (3.6).

Integrating (3.12) using (3.13), we find

$$\phi_t + \frac{\partial}{\partial z}\left[\phi u - \int_0^\infty fv_s \, da\right] = 0. \tag{3.15}$$

In addition, conservation of liquid mass takes the form

$$-\phi_t + \frac{\partial}{\partial z}[(1 - \phi)u] = 0, \tag{3.16}$$

and from these last two equations we obtain

$$u = \int_0^\infty fv_s \, da, \tag{3.17}$$

assuming no net volume flux. Using this in (3.15) and putting $z = -Z$, we obtain the evolution equation for ϕ,

$$\phi_t + \frac{\partial}{\partial Z}\left[(1 - \phi)\int_0^\infty fv_s \, da\right] = 0, \tag{3.18}$$

while for f, (3.12) implies

$$f_t + \frac{\partial}{\partial Z}\left[f\left\{v_s - \int_0^\infty f v_s \, da\right\}\right] = 0. \tag{3.19}$$

In general, this equation requires numerical solution. Simplifications are possible for two grain sizes, or for dilute suspensions ($\phi \ll 1$), for which also $fa \ll 1$, and the integral term can be dropped from (3.19); in this case the particles fall independently of each other, and the time for settlement is determined entirely by particle size.

0.4   Movement of the glass

We finally consider under what conditions the rinsing will cause a glass to lift from its base.

The glass is sitting on an oscillating slatted base (figure 3.) The flow at ∞ is also oscillating.

Figure 3: Position of glass in basket

Let $v = \alpha \epsilon e^{i\omega t}(i\omega)$ at ∞. (α could be complex.) We assume the flow is inviscid and linearise.

Equation for glass

$$m\ddot{z} = -mg + L + R \tag{4.1}$$

where L is fluid lift and (see figures 4 and 5)

$$R = 0, \quad \text{if } z > \epsilon \cos \omega t$$
$$> 0, \quad \text{if } z = \epsilon \cos \omega t$$

Glass resting on the shelf

$$z = \varepsilon \cos\left(\omega t\right)$$
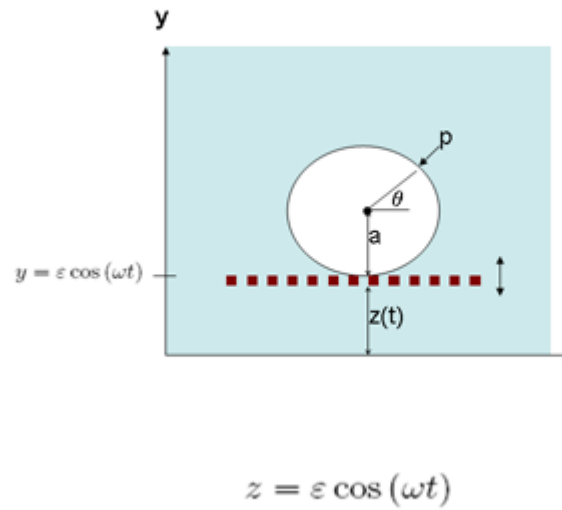
Figure 4:

Glass separated from the shelf

$$z > \varepsilon \cos\left(\omega t\right)$$

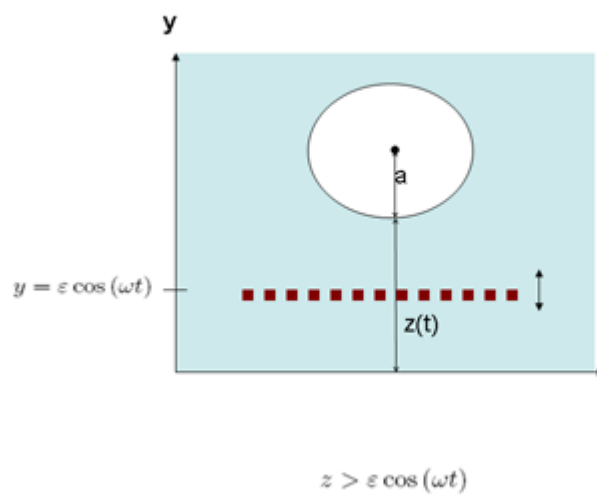Figure 5:

$$\phi = (i\omega)\alpha\epsilon e^{i\omega t}(r\sin\theta + \frac{a^2}{r}\sin\theta) - \dot{z}\frac{a^2}{r}\sin\theta \tag{4.2}$$

$$\text{Lift on cylinder} \quad = \quad -\int_0^{i\pi} p\sin\theta a\,d\theta$$

$$= \quad +\rho\int_0^{i\pi}(\phi_t + g(a + z + r\sin\theta)a\sin\theta\,d\theta$$

$$= \quad \rho a[-a\pi\ddot{z} + ga\pi + 2a\pi\epsilon\alpha(i\omega)^2 e^{i\omega t}]$$

When glass is in contact $z = \epsilon e^{i\omega t}$ and so

$$R \quad = \quad m\ddot{z} + mg + \pi a^2\rho\ddot{z} - \pi a^2\rho g + 2\rho a^2\pi\epsilon\alpha\omega^2 e^{i\omega t}$$

$$= \quad (m + \bar{m})\ddot{z} + (m - \bar{m})g + 2\rho a^2\pi\epsilon\alpha\omega^2 e^{i\omega t}$$

$$= \quad -\epsilon\omega^2(m + \bar{m})e^{i\omega t} + (m - \bar{m})g + 2\rho a^2\pi\epsilon\alpha\omega^2 e^{i\omega t}$$

where $\bar{m} = \rho\pi a^2$ is the mass of fluid displaced by the object. Thus

$$R = -\epsilon\omega^2(m + \bar{m})\cos\omega t + (m - \bar{m})g + 2\epsilon\bar{m}\omega^2(\alpha_r\cos\omega t - \alpha_i\sin\omega t) \tag{4.3}$$
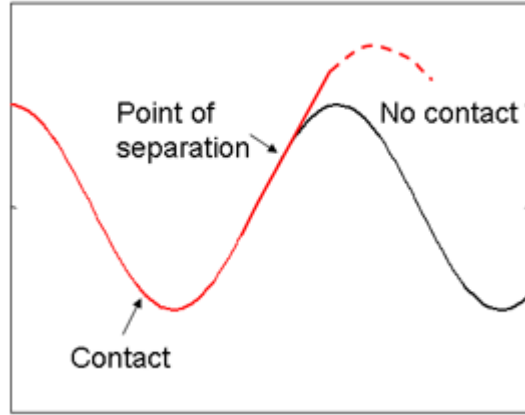
We can now consider two cases.

Figure 6:

0.4.1 Case 1.

First consider $\alpha = 0$; i.e., there is no flow at ∞.

$R = 0$ when $\cos\omega t = \frac{(m-\bar{m})g}{(m+\bar{m})\epsilon\omega^2}$; i.e., the glass will rise from the support if

$$\epsilon\omega^2 > \left(\frac{m - \bar{m}}{m + \bar{m}}\right)g \tag{4.4}$$

$m =$ mass of glass + water ≈ 920 grams. $\bar{m} =$ added mass $=$ water displaced by glass and water ≈ 650 grams; i.e., we need $\epsilon\omega^2 > \frac{270}{1570}g$ or (using $\epsilon = 0.05$)

$$\omega^2 > \frac{270}{157} \times 20 \approx 34.39 \tag{4.5}$$

Thus, if $\omega > 6$ the glass will lift. The actual $\omega \approx 40$ cycles/min ≈ 4 rad/sec.

0.4.2   Case 2.

Now let $\alpha_r = 1$, $\alpha_i = 0$; i.e., flow at ∞ moves with the cage
    $R = 0$ when

$$\epsilon\omega^2(\bar{m} - m)\cos\omega t + (m - \bar{m})g = 0;$$

i.e., if $\epsilon\omega^2\cos\omega t = g$, which can happen only if $\epsilon\omega^2 > g$ (which is less likely).