Dissolution of diesel exhaust in seawater

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We consider a large container ship discharging its diesel-engine exhaust in the form of small bubbles some depth beneath the surface of the ocean.

1 Bubble velocity

We first determine the terminal upward velocity of bubbles of a particular size. For simplicity, we assume that the CO_2 dissolves relatively rapidly, so that the pressure and volume of the bubbles remain constant over the relevant portion of their trajectory. This assumption will be justified below. We also assume (somewhat incorrectly) that the bubbles are spherical. Then they experience a buoyant force

$$F_B = \Delta\rho g V = \frac{4}{3}\Delta\rho g A r,$$

where $\Delta\rho$ is the difference in density between the bubble and the water, g is the acceleration due to gravity, V is the volume, A is the cross-sectional area, and r is the bubble radius. Even at $h = 100\,\mathrm{m}$, the bubble density is small enough that we can pretend that $\Delta\rho = \rho$, where $\rho \approx 1027\,\mathrm{kg\,m^{-3}}$ denotes the density of seawater at $283\,\mathrm{K}$, a typical temperature for surface seawater [6]. The drag experienced by the bubble is

$$F_D = \frac{1}{2}C_D \rho A v^2,$$

where C_D is the drag coefficient for a sphere and v is the bubble velocity.

Empirically, the drag coefficient C_D is a function of two dimensionless constants: the Reynolds number $\mathrm{Re} := \frac{2vr}{\nu}$ and the Eötvös number $\mathrm{Eo} := \frac{4\Delta\rho g r^2}{\sigma}$, where $\nu = 1.36 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$ is the kinematic viscosity of seawater and $\sigma = 7.6 \times 10^{-2}\,\mathrm{N\,m}$ is the surface tension [6]. The Reynolds number quantifies the balance between viscous and convective forces, while the Eötvös number expresses the balance between buoyancy and surface tension. The former is clearly relevant to drag; the latter determines the shape of the bubble.

Tomiyama et al. [8] found the following empirical expression for C_D, which is valid over a useful range of parameters ($10^{-3} < \mathrm{Re} < 10^5$ and $10^{-2} < \mathrm{Eo} < 10^3$):

$$C_D = \max\left\{\frac{24}{\mathrm{Re}}\left(1 + 0.15\,\mathrm{Re}^{0.687}\right),\ \frac{8}{3}\frac{\mathrm{Eo}}{\mathrm{Eo}+4}\right\}.$$

To determine the terminal velocity, we set $F_B = F_D$ and solve for v. Since Re depends on v, this must be done numerically. The results replicate Fig. 3 in Olsen et al. [6], who study small CO_2 bubbles rising in seawater. This figure agrees well with experimental data presented in Fig. 2 of Johnson et al. [5].

For a typical bubble radius of 1 mm, we find $v = 0.19\ \mathrm{m\,s^{-1}}$. We assume that the bubble instantly attains its terminal velocity.

2 CO_2 dissolution

Setting up a general mass transfer problem, the mass flux Φ through the bubble's surface is proportional to the difference in concentration between the bubble surface and infinity. Since our CO_2 partial pressures are 100× atmospheric, we approximate the CO_2 concentration far from the bubble (i.e. in ambient seawater) as 0. Then $\Phi = kc$, where k is the mass transfer constant and c is the concentration of CO_2(aq) at the bubble surface. We note that Φ has the units $\mathrm{mol\,m^{-2}\,s^{-1}}$. The diffusivity of CO_2(g) in N_2(g) is much higher than CO_2(aq) in H_2O, so we can assume a uniform CO_2 concentration in the bubble interior. Also, our exhaust is 95% N_2, so we can approximate its volume as constant as the CO_2 leaves. Thus the radius is held fixed through all our calculations.

If c_g denotes the molar concentration of CO_2 in the bubble gas, we have

$$n = \frac{4}{3}\pi r^3 c_\mathrm{g} \quad \text{and} \quad \dot{n} = -4\pi r^2 \Phi,$$

where n denotes the amount of CO_2(g) in the bubble in moles. Since the radius is constant in time, we can rearrange to find

$$\dot{c}_\mathrm{g} = -\frac{3\Phi}{r}.$$

Now, the gaseous concentration c_g is related to the aqueous concentration c at the surface of the bubble by Henry's law:

$$c = Hc_\mathrm{g}, \tag{1}$$

where $H = 1.27$ is the dimensionless Henry solubility at 283 K. Gathering everything together, we have

$$\dot{c} = H\dot{c}_{\mathrm{g}} = -\frac{3H\Phi}{r} = -\frac{3Hk}{r}c. \tag{2}$$

Next, we determine the mass transfer constant k. This constant is commonly expressed in terms of the dimensionless Sherwood number $\mathrm{Sh} := \frac{2rk}{\mathcal{D}}$, where $\mathcal{D} = 1.28 \times 10^{-9}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ is the mass diffusivity of CO_2 in seawater [6]. In turn, the Sherwood number is often viewed as a function of the Reynolds number Re and the *Schmidt number* $\mathrm{Sc} := \frac{\nu}{\mathcal{D}} = 1065$.

As it happens, our system lies on the boundary of two well-known regimes. In the *immobile* regime, surfactants crowd the surface of the bubble, immobilizing the fluid at the boundary. This reduces the shear and Sh. In the *mobile* regime, the fluid flow is strong enough to continually flush away surfactants. The bubble surface is thus mobile, leading to higher shear and Sh.

These two regimes are often named after Frössling and Higbie, respectively, who first provided theoretical descriptions. The immobile regime is difficult to describe analytically; instead, various empirical relationships have been proposed. Data of Olsen et al. support an approximation they attributed to Hughmark [4] but originally due to Garner and Suckling [2]:

$$\mathrm{Sh}_{\mathrm{im}} = 2 + 0.95\,\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}. \tag{3}$$

The mobile regime has a simple analytical expression due to Higbie [3]:

$$\mathrm{Sh}_{\mathrm{m}} = \frac{2}{\sqrt{\pi}}\left(\mathrm{Re}\mathrm{Sc}\right)^{1/2}. \tag{4}$$

Experimental data of [1] suggest that CO_2 bubbles in water transition from the immobile to mobile regime between the radii $r_1 := 1\,\mathrm{mm}$ and $r_2 := 2\,\mathrm{mm}$. For simplicity, we linearly interpolate between $\mathrm{Sh}_{\mathrm{im}}$ and Sh_{m} in this range:

$$\mathrm{Sh} = \begin{cases} \mathrm{Sh}_{\mathrm{im}} & \text{if } r < 1\,\mathrm{mm} \\ \frac{r_2 - r}{r_2 - r_1}\mathrm{Sh}_{\mathrm{im}} + \frac{r - r_1}{r_2 - r_1}\mathrm{Sh}_{\mathrm{m}} & \text{if } 1 \le r \le 2\,\mathrm{mm} \\ \mathrm{Sh}_{\mathrm{m}} & \text{if } r > 2\,\mathrm{mm} \end{cases} \tag{5}$$

We note that the regime makes a big difference: $\frac{\mathrm{Sh}_{\mathrm{m}}}{\mathrm{Sh}_{\mathrm{im}}} \approx 3.7$ when $r = 1.5\,\mathrm{mm}$.

Using (2), we have

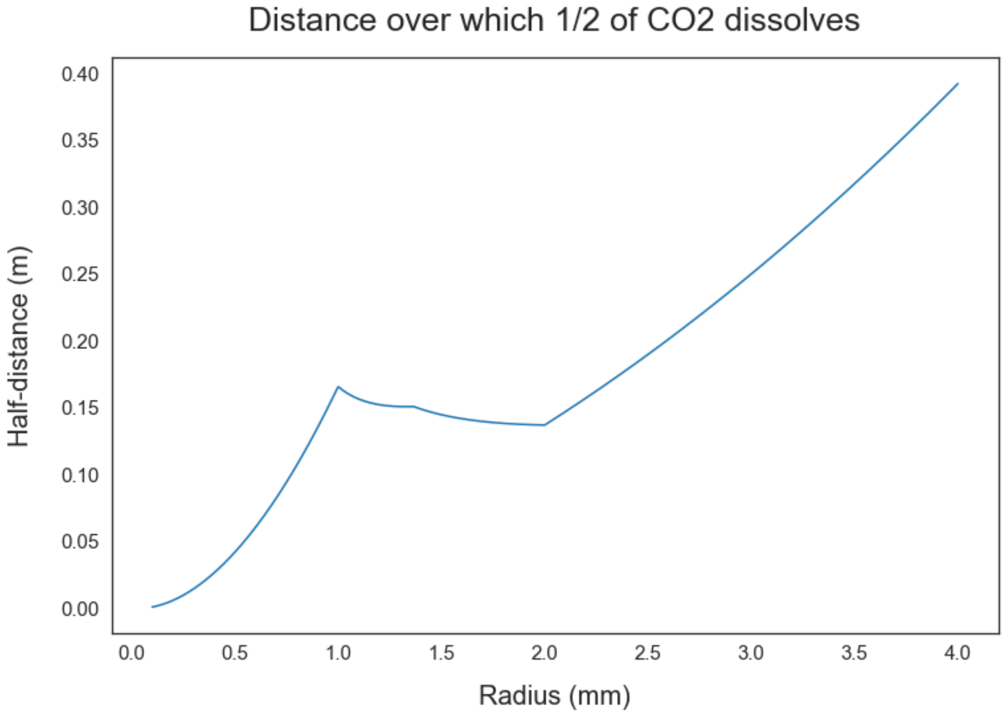
$$\dot{c} = -\frac{3\mathrm{Sh}H\mathcal{D}}{r^2}c.$$

Thus, the concentration c (and, proportionally, the amount n) decreases exponentially with rate constant $\lambda := \frac{3\mathrm{Sh}H\mathcal{D}}{r^2}$. Using the terminal velocity v computed earlier, we can find the Reynolds number Re, and thus the Sherwood number Sh. As we shall see, our estimate lies within 40% of the experimental results we could find. We therefore keep one significant digit.

For 1 mm bubbles, we find $\mathrm{Re} = 300$, $\mathrm{Sh} = 200$, and $\lambda = 0.8\,\mathrm{s}^{-1}$. Thus

$$c(t) = c(0)\mathrm{e}^{-\lambda t} \quad \text{for } \lambda = 0.8\,\mathrm{s}^{-1}.$$

This corresponds to a half-life of $t_{1/2} = 0.9$ s for the CO_2 in the bubble. During this time, the bubble rises a distance $d_{1/2} := vt_{1/2} = 0.2\,\mathrm{m}$. That's quite short, justifying our assumption of constant pressure. We plot this "half-distance" $d_{1/2}$ over a reasonable range of bubble sizes:



3 Experimental validation

We compare these estimates against four sets of experimental results for CO_2 in water: two for small bubbles, and two for large.

Olsen et al. [6] study CO_2 in *sea*water, so this is the closest analogue to our setting. They do not estimate k or Sh explicitly, but they do find evidence that bubbles with $r \leq 400\,\mu\mathrm{m}$ are immobile and modeled best by (3). They remark: "Due to the high solubility of CO_2, the bubbles are depleted of CO_2 within seconds."

Takemura and Yabe [7] also study bubbles of radii under $500\,\mu\mathrm{m}$. They find the bubbles to be immobile, but provide a different empirical relationship than (3). Our expression is 40% higher than theirs at the upper end of their size range, where the discrepancy is largest.

Deindorfer and Humphrey [1] study larger bubbles ($0.6 \leq r \leq 3\,\mathrm{mm}$) over long durations. They find a transition from mobile to immobile behavior over the lifetime of the bubbles, perhaps attributable to the accumulation of surfactants. We make a quantitative comparison with the measurement of k listed in Table II [1]. Our approximation is 40% lower than their measurement.

Finally, Johnson et al. [5] study large bubbles ($2 \leq r \leq 10\,\mathrm{mm}$). Their data indicate that the bubbles are mobile, and they find an empirical relationship for Sh similar to (4). Our approximation is 15% higher than their model.

On the whole, the expression (5) appears to capture the mass-transfer characteristics of CO_2 bubbles in water to within 40% over a wide range of radii.

4 Saturation

Above, we considered a single bubble rising through an unperturbed sea. Next, we consider seawater that has equilibrated with the CO_2 in diesel exhaust. This exhaust is roughly 5% CO_2. At a depth of 40 m, that corresponds to a partial pressure of $2 \times 10^5\,\mathrm{Pa}$, and $c_\mathrm{g} = 8.7 \times 10^{-3}\,\mathrm{M}$. Using (1), we have $c = 1.2 \times 10^{-2}\,\mathrm{M}$. The equilibrium constant for dissociation to bicarbonate is

$$K = \frac{[\mathrm{H}^+]\,[\mathrm{HCO_3}^-]}{[\mathrm{CO_2(aq)}]} = 3.0 \times 10^{-7}\,\mathrm{M}.$$

Equilibrium with this much CO_2 will be rather acidic, so very little carbonate will be present. We thus neglect the second dissociation of CO_2. If the CO_2 were dissolving in pure water, we would have

$$[\mathrm{HCO_3}^-] = \sqrt{K[\mathrm{CO_2(aq)}]} = 6.0 \times 10^{-5}\,\mathrm{M}.$$

However, the ambient concentration of bicarbonate in seawater is $2.2 \times 10^{-3}\,\mathrm{M}$. This is thus a heavily buffered solution, and we don't expect the concentration of bicarbonate to change much.

Assuming this, the *increase* in bicarbonate concentration is

$$\Delta[\mathrm{HCO_3}^-] = \frac{K[\mathrm{CO_2(aq)}]}{[\mathrm{HCO_3}^-(\mathrm{sea})]} = 1.58 \times 10^{-6}\,\mathrm{M}.$$

This is minuscule compared to $[\mathrm{CO_2(aq)}] = c = 1.2 \times 10^{-2}\,\mathrm{M}$. Thus the dissolved inorganic carbon at equilibrium is dominated by the dissolved $\mathrm{CO_2}$.

A typical 10^5 DWT container ship produces $6 \times 10^6\,\mathrm{m^3\,day^{-1}}$ of exhaust. Using Henry's law (1), this corresponds to $4.3 \times 10^6\,\mathrm{m^3\,day^{-1}}$ of seawater at equilibrium with the exhaust. At 60% load, the ship displaces $6 \times 10^4\,\mathrm{m^3}$ of water, so if it left behind fully saturated water, its exhaust would fill its own displaced volume every 20 min. If the ship is 350 m long and traveling at 16 knots, it moves through its displaced volume in 41 s. Thus under typical steaming, the ship will not come close to saturating the surrounding water.

References

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