Bubble nucleation in supersaturated liquids

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For dilute solutions, Henry’s law states

\[
\left\{ \begin{array}{l}
\text{dissolved gas concentration} \\
\text{partial pressure}
\end{array} \right\} \propto \Rightarrow c = kp \quad \text{(dilute solution)}
\]

where \( k \) is an empirical ‘constant’. E.g., carbonated drinks, decompression sickness,...

- \( k \downarrow \) as temperature \( T \uparrow \). E.g., thermal pollution of lakes, exploding glass bottles,...
In a sealed bottle the total mass $m$ of gas is constant:

$$m = cV_L + \rho_G V_G$$

$$\Rightarrow m = kpV_L + \frac{p}{R_s T} V_G \text{ (ideal gas)}$$

$$\Rightarrow p = \frac{m}{k(T) V_L + \frac{1}{R_s T} V_G}$$

As $T \uparrow$, $k \downarrow$ and thus $p \uparrow$. 

$k*p^*V_L$
Henry’s law: effect of heating a sealed carbonated drink

For $\text{CO}_2$ and $V_G / V_L = 1/9$, $V_L + V_G = 0.5 \text{ L}$:

$$p = \frac{m}{(0.45 \text{ L}) k(T) + \frac{0.05 \text{ L}}{\left(189 \text{ J kg}^{-1} \text{ K}^{-1}\right) T}}$$

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>0</th>
<th>8</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (g L$^{-1}$ bar$^{-1}$)</td>
<td>3.42</td>
<td>2.50</td>
<td>2.05</td>
<td>1.76</td>
</tr>
<tr>
<td>$p$ (bar)</td>
<td>2</td>
<td>2.68</td>
<td>3.23</td>
<td>3.71</td>
</tr>
<tr>
<td>$c = kp$ (g L$^{-1}$)</td>
<td>6.84</td>
<td>6.71</td>
<td>6.61</td>
<td>6.53</td>
</tr>
</tbody>
</table>
Exploding bottles of carbonated drinks

- Experimental results for 2 L PET bottles:

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Mean pressure (bar)</th>
<th>Max pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 °C</td>
<td>3.20</td>
<td>3.86</td>
</tr>
<tr>
<td>15 °C &amp; agitation</td>
<td>3.33</td>
<td>3.86</td>
</tr>
<tr>
<td>20 – 39 °C</td>
<td>3.81</td>
<td>4.55</td>
</tr>
<tr>
<td>40 – 59 °C</td>
<td>4.03</td>
<td>4.76</td>
</tr>
<tr>
<td>40 – 59 °C &amp; agitation</td>
<td>5.94</td>
<td>8.14</td>
</tr>
</tbody>
</table>


Lesson of the Week

Ocular injuries due to exploding bottles of carbonated drinks

P W Sellar, P B Johnston
Ginger ale
Opening the bottle: supersaturated liquids

- When a bottle is opened, the pressure drops.
- Solution is now supersaturated, $c > kp$.
- To satisfy Henry’s law, $c = kp$, $c$ must decrease.
- Gas can diffuse out or form bubbles, if it can...
- We want bubbles!
Pressure inside bubbles: Young-Laplace law

- Surface tension $\gamma = \text{force per unit length (exerted by one surface)} \ (N\ m^{-1})$.

- Forces on hemisphere:
  - Force to the left $= \gamma 2\pi R$
  - Force to the right $= (p_i - p_o) \pi R^2$
  - For equilibrium $(p_i - p_o) \pi R^2 = \gamma 2\pi R$

  \[ p_i - p_o = \frac{2\gamma}{R} \]

- E.g., liquid drops, gas bubbles in liquid
For a soap bubble, the film has two surfaces.

Forces on hemisphere:
- Force to the left = \[2 \times \gamma 2\pi R\]
- Force to the right = \[(p_i - p_o) \pi R^2\]
- For equilibrium \[(p_i - p_o) \pi R^2 = \gamma 4\pi R\]

\[\Rightarrow p_i - p_o = \frac{4\gamma}{R}\]
Given a bubble of radius $R$, does it shrink or grow?

- A bubble is in equilibrium if Henry’s law is satisfied:
  \[ c = k \rho_B \]

- Bubble shrinks if $c < k \rho_B$; bubble grows if $c > k \rho_B$.

- Using Young-Laplace law,
  \[ c = k \left( p_L + \frac{2 \gamma}{R} \right) \]
Bubbles with radii greater than the critical radius grow

- Solving for $R$ yields

\[ R = \frac{2\gamma}{c/k - p_L} \equiv R_c \]

- Bubble shrinks if $R < R_c$ ($c < kp_B$); bubble grows if $R > R_c$ ($c > kp_B$).

- Can decrease $R_c$ by
  - decreasing $\gamma$ or $p_L$
  - increasing $c$

- For an open bottle $p_L \approx p_a$. 

\[ R_c = \frac{2\gamma}{c/k - p_a} \]
How liquid pressure affects the critical radius
But do bubbles with $R > R_c$ form in a supersaturated liquid?

- Bubbles with $R > R_c$ will only form in the bulk of a pure liquid if the dissolved gas concentration $c$ is $\sim 100$ times higher than it is in beverages (homogeneous nucleation).

<table>
<thead>
<tr>
<th>Beverage</th>
<th>$\gamma$ (mN m$^{-1}$)</th>
<th>$p$ (bar)</th>
<th>$c$ (g L$^{-1}$)</th>
<th>$c$ (Vol.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Champagne (12°C)</td>
<td>47</td>
<td>6</td>
<td>11.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Carbonated beers (8°C)</td>
<td>44</td>
<td>1.6 – 2.4</td>
<td>4 – 6</td>
<td>2 – 3</td>
</tr>
<tr>
<td>Soft drinks (8°C)</td>
<td>74</td>
<td>1.6 – 4</td>
<td>4 – 10</td>
<td>2 – 5</td>
</tr>
<tr>
<td>Guinness (CO$_2$) (8°C)</td>
<td>40</td>
<td>0.8</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Guinness (N$_2$) (8°C)</td>
<td>40</td>
<td>3.0</td>
<td>0.07</td>
<td>0.06</td>
</tr>
</tbody>
</table>

- Why then do bubbles form in these beverages? Because the bubbles actually form at nucleation sites on the glass surface.
- Or, if poured sloppily, because air bubbles are entrained into the liquid.
Bubbles need nucleation sites: heterogeneous nucleation

- Trapped air pockets with $R > R_c$ can grow into bubbles.
- Air can become trapped in crevices, fibres, or salt crystals on a glass surface as liquid is being poured.
- E.g., soft drink & ice/Mentos/salt/sugar...
Heterogeneous nucleation: crevices as nucleation sites

Bubble production cycle:

1) Dissolved gas diffuses into trapped air pocket
2) Bubble forms
3) And grows until
4) Bubble detaches
10 grams of polystyrene granules initiate (i.e., foam) Guinness
Heterogeneous nucleation: fibres as nucleation sites

Bubble production cycle:

1) Dissolved gas diffuses into trapped air pocket
2) Pocket reaches tip of fibre
3) Bubble grows
4) Bubble detaches
Heterogeneous nucleation: fibres as nucleation sites
When does bubble production stop?

- As $c$ decreases, $R_c$ increases.
- Eventually, radius of gas pocket is equal to the critical radius and bubble production stops.

$$R_c = \frac{2\gamma}{(c/kp_a)}$$
Contains dissolved carbon dioxide & nitrogen.

Why nitrogen? As foam is ‘creamier’ (smaller bubbles) and lasts much longer.

\[ c_{CO_2} = k_{CO_2} p_{CO_2} = (2.5 \text{ g L}^{-1} \text{ bar}^{-1})(0.8 \text{ bar}) = 2 \text{ g L}^{-1} \]

\[ c_{N_2} = k_{N_2} p_{N_2} = (0.0241 \text{ g L}^{-1} \text{ bar}^{-1})(3.0 \text{ bar}) = 0.072 \text{ g L}^{-1} \]

Since \( c_{CO_2} < k_{CO_2} p_a = (2.5 \text{ g L}^{-1} \text{ bar}^{-1})(1 \text{ bar}) = 2.5 \text{ g L}^{-1} \), pure CO\(_2\) bubbles cannot form, i.e., there must be some nitrogen in each bubble.

When nitrogen runs out, bubble growth stops.

Problem: Guinness does not bubble/foam spontaneously but must be ‘initiated’.

The rate of bubble production from crevices and fibres is very slow (practically zero). Adding sugar/salt works though...
Sweet Stout

- Murphy’s Draught Stout & 1 heaped desertspoon sugar.
Salty Stout

- Murphy’s Draught Stout & 1 heaped dessertspoon salt.
- Smaller bubbles, longer to settle, bigger head.

Before

After
Guinness: initiation/foaming methods

We can either

1. grow existing precritical \((R < R_c)\) bubbles by decreasing \(R_c = \frac{2\gamma}{c/k-p_L}\) to make them postcritical.

2. inject postcritical \((R > R_c)\) bubbles which can then grow by absorbing dissolved gas.

Some initiation methods

1. Polystyrene granules (supplies trapped air pockets with \(R > R_c\)...)
2. Restrictor plate (pressure drop decreases \(R_c\), cavitation and turbulence creates bubbles...)
3. Surger (pressure oscillations vary \(R_c\)...)
4. Widget (injects postcritical bubbles...)

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Guinness flows through a five-hole restrictor plate in the stout faucet.

Conservation of mass:

\[ \rho v A = \text{const} \]

\( A \downarrow, \quad v \uparrow \)

Bernoulli’s principle:

\[ \frac{1}{2} \rho v^2 + p + \rho gz = \text{const} \]

\( v \uparrow, \quad p \downarrow \)

By oscillating the glass & Guinness, bubbles with $R < R_c$ can be made to grow rather than shrink.

- $p_L = p_a + P \sin(\omega t)$
- $\omega = 2\pi f$, $f$ ultrasonic
Surger: mechanism

- Gas diffuses out when bubble compresses ($p_L \uparrow$, $R \downarrow$, $R_c \uparrow$) and in when expands ($p_L \downarrow$, $R \uparrow$, $R_c \downarrow$).
- But surface area and concentration gradient greater during expansion so net effect is that bubble grows (if pressure amplitude above a certain threshold).
Widget: many patents...


US Patent 6,896,920 (2005)
Conclusions

- Gas solubility decreases as temperature increases.
- Only bubbles above a critical size ($R_c$) grow.
- Homogeneous nucleation of postcritical ($R > R_c$) bubbles doesn’t happen.
- Heterogeneous nucleation from trapped gas pockets can happen.
- Guinness uses nitrogen to achieve a creamy, long-lasting head.
- But Guinness doesn’t foam spontaneously.
- Initiation methods: polystyrene granules, restrictor plate, surger, widgets.
- Cheaper initiation methods that are reliable needed.