13.6 Rate Constants for Coalescence

Demonstrate that when two bubbles of equal size coalesce, the resulting equilibrium bubble volume is > twice the single bubble volume.

\[
m = \left( \frac{4 \pi R^3}{3} \right) \sum \left( \frac{2 \gamma}{R k T} \right)
\]

\[
\frac{m_f}{m_o} = \frac{R_f^2}{R_0^2}
\]

\[
\frac{(\Delta V/V)_f}{(\Delta V/V)_0} = 2^2 \times \frac{1}{2} = \sqrt{2}
\]

Analysis of bubble coalescence in the Absence of temperature or stress gradients

a.) First consider a fixed bubble radius R being bombarded by moving bubble of radius R. This gives;

\[
Rate = 4 \pi (2R) D_b \left[ 1 + \frac{2R}{\sqrt{\pi D_b t}} \right] C_m
\]
where;
\[ C_m = \text{# of bubbles containing m gas atoms} \]

b.) If we allow all bubbles to move;

\[
\text{Rate} = 4\pi (2R) 2D_b \left[ 1 + \frac{2R}{\sqrt{\pi 2D_b t}} \right] C_m
\]

c.) Rate of collision between bubbles containing m \( \frac{\text{atoms}}{\text{cm}^3} \);

\[
\text{Rate} = 4\pi (2R) 2D_b \left[ 1 + \frac{2R}{\sqrt{\pi 2D_b t}} \right] C_m^2
\]

d.) More general expression for bubbles of size j and size i;

\[
\text{Rate Constant}
\]

\[
k_{ij} = 4\pi (R_i + R_j) \sum (D_{bi} + D_{bj})
\]

\[
\text{Rate} = 4\pi (R_i + R_j) \sum (D_{bi} + D_{bj}) \left\{ 1 + \frac{(R_i + R_j)}{\sqrt{\pi (D_{bi} + D_{bj}) t}} \right\} C_i C_j
\]

Neglect when migration distance between collisions is large compared to bubble radii

5.) Include Stress or Temperature Gradients
(Biased Effects)

(see figure 13.10)

Rate at which bubbles of size i coalesce with size j in time t;

\[ k_{ij} = \pi (R_i + R_j)^2 (v_{bi} - v_{bj}) C_i \]

But since there are \( C_j \) \( \frac{\text{bubbles}}{\text{cm}^3} \);

\[ k_{ij} = \pi (R_i + R_j)^2 (v_{bi} - v_{bj}) \]

Problem 13.4

13.7 Bubble Resolution

Macroscopic Models

- Ross - Thermal Spike
- Whapham - Chunk
- Turnbull - Destroy Bubbles

Microscopic

- Nelson - single atom resolution
- Manley - single atom resolution

Turnbull
Fig. 13.10  Diagram for computing the coalescence rate for biased bubble motion.

Fig. 13.11  Diagram for calculating the re-solution parameter by Turnbull's method. [After J. A. Turnbull, J. Nucl. Mater., 38: 203 (1971).]
Problem 13.4

Assume only 2 groups of bubbles in fuel

\[ r_1 \text{ and } r_2 = 0.5 \ r_1 \]

which are in equilibrium \( \frac{2\gamma}{r} \), with no external pressure. Let bubbles migrate in random manner and when collisions occur, (only one bubble with any other one bubble),

**What is the swelling \( \frac{\Delta V}{V} \) due to this process?**

Initially, Type I \( P_1 = \frac{2\gamma}{r_1} \)

Type II \( P_2 = \frac{4\gamma}{r_1} \)

Volume of bubbles \( = \frac{4}{3} \pi n (r_1^3 + r_2^3) \)

\( n = \text{number of bubbles of each type (2n total)} \)

Using ideal gas law, let \( N_i \) be the number of gas atoms in the bubble of type \( i \):

\[ N_i = p_i \left( \frac{4\pi r_i^3}{3kT} \right) = \frac{4\pi}{3} \left( \frac{2\gamma}{kT} \right) r_i^2 \quad i=1,2 \]
We have 3 types of collisions;

\[
\begin{align*}
&I + I \\
&I + II \\
&II + I \\
&II + II
\end{align*}
\]

Note: Because of higher diffusivity of smaller bubbles, we can not get explicit expressions for coalescence.

Assume that the probability of each type of collision is the same \( \approx \frac{1}{4} \)

We finish with \( n \) total bubbles:

\[
\begin{align*}
\frac{n}{4} & \text{ bubbles of type } I + I \\
\frac{n}{4} & \text{ bubbles of type } II + II \\
\frac{n}{2} & \text{ bubbles of type } I + II, II + I
\end{align*}
\]

Moles of gas in bubbles (or # of gas atoms)

\[
N = N_i + N_j = \frac{4\pi}{3} \left( \frac{2\gamma}{kT} \right) \left( r_i^2 + r_j^2 \right)
\]

For an ideal gas

\[
p = \frac{2\gamma}{r}
\]
\[ p \left( \frac{4\pi r^3}{3} \right) = NkT \]
\[ \therefore r = \frac{2\gamma}{p} = 2\gamma \left( \frac{4\pi r^3}{3NkT} \right) \]

This gives \( r = \sqrt{r_i^2 + r_j^2} \)

**Final volume of gas**

\[
V = \frac{4\pi n}{3} \left\{ \frac{1}{4} (r_1^2 + r_1^2)^3 + \frac{1}{4} (r_2^2 + r_2^2)^3 + \frac{1}{2} (r_1^2 + r_2^2)^2 \right\}
\]

**Swelling** = \( \left( \frac{V - V_{\text{initial}}}{V_{\text{initial}}} \right) = \frac{V}{V_{\text{initial}}} - 1 \)

\[
V_{\text{initial}} = \frac{4\pi n}{3} (r_1^3 + r_2^3)
\]

\[
\text{Swelling} = \frac{1}{\sqrt{2}} (r_1^3 + r_2^3) + \frac{1}{2} (r_1^2 + r_2^2)^2 - 1
\]

but \( r_2 = 0.5 \ r_1 \)

\[
\frac{\Delta V}{V} = \frac{1}{\sqrt{2}} + \frac{r_2^3}{r_2^3 (1 + 8)} - 1 = 0.328
\]
Gas bubbles destroyed \( \frac{\text{cm}^3 \cdot \text{sec}}{} = b'C_m \)

\( b' = \text{prob/s that a bubble in fuel is destroyed.} \)

\[ = 2\pi R^2 \mu_{ff} \sum F \]

Gas atoms returned to the matrix from bubble per \( \text{cm}^3 \) and per second. = \( b'm \) \( N \)

bubbles/cm\(^3\) which contain \( m \) gas atoms

Need several things;
1.) Flux of FF’s
2.) Energy of FF’s
3.) Cross section for interaction (usually Coulomb)
4.) Energy of gas atom that can make it out of the bubble

gas atoms returned to matrix from bubbles

\[ cm^3 \text{ sec} \]

\[ = bmN \]

Where

\[ b = \frac{2\pi Z^4 e^4}{E_{ff}T_{\min}} \ln \left( \frac{E_{ff}^{\max}}{T_{\min}} \right) \mu_{ff} \sum F \]

in fact, even this is too small and Nelson includes the interaction between the PKA’s and gas atoms in the bubble to get results which are closer to experiment.

Nelson found that the efficiency of pushing gas atoms back into the matrix varies from 44% for very large bubbles to 100% when diameters are \( \approx 30 \text{ Å} \).
13.8 Nucleation of Fission Gas Bubbles

First distinction is between nucleation.
- Homogeneous
- Heterogeneous

-------------------------------

13.8.1 Homogeneous Nucleation

Assume stable nuclei are diatomic cluster of gas atoms, see figure 13.12

Define 1.) Nucleation time \( \left( \frac{\partial C_2}{\partial t} = 0 \right)_{t_c} \)
2.) Nucleation density, \( C_2 \) at \( t_c \)
3.) Note; assume constant concentration of bubbles after \( t_c \)

Sequence
\[
\frac{dC}{dt} = Y_{xe} \sum F - 2k_{11}C^2 - k_{12}CC_2
\]
Fission --> \( g \)
Conc. of 2 consumed Triatomic
\( g + g <==> g_2 \) single gas per diatomic atoms
\( g + g_2 <==> g_3 \)
\[-k_{lm}CC_m + 2(2C_2)b + ... + mC_mb \]

.............
\( g + g_m <==> g_{m+1} \) Assumes whole bubble dissolved

note; only simple gas atoms added, not clusters.
For diatomic clusters
Figure 13.12 - Variation of Matrix gas atom and two- and three-atom clusters during irradiation.
\[
\frac{dC_2}{dt} = k_{11}C_2^2 - k_{12}CC_2 - (2C_2)b + (3C_3)b + \ldots
\]

in general,

\[
\frac{dC_m}{dt} = k_{1,m-1}CC_{m-1} - k_{1m}CC_m - (bmC_m) + (m+1)C_{m+1}b
\]

Balance on gas atoms:

\[
Y_{Xe} F = \frac{dC}{dt} + 2\frac{dC_2}{dt} + \ldots + m\frac{dC_m}{dt}
\]

---------------------------

Use the above analysis to determine the concentration of single and diatomic gas atom clusters at the end of the nucleation period, \(t_c\).

\[
Y_{Xe} F = \left(\frac{3k_{11}k_{12}C_c^3}{k_{12}C_c + 2b}\right)
\]

Growth by Resolution addition

and \(C_{2c} = \frac{k_{11}C_c^2}{(k_{12}C_c + 2b)}\)

Figure 13.13
Fig. 13.13 The homogeneous nucleation function (with re-solution).
at high temperatures and low fission rates;

\[ C_c = \sqrt[3]{\frac{Y_{Xe} F}{3k_{11}}} \]

\[ C_{2c} = \sqrt[3]{\frac{Y_{Xe} F k_{11}}{3k_{12}^2}} \]

at low temperatures and high fission rates;

\[ C_c = \left( \frac{2bY_{Xe} F}{3k_{11}k_{12}} \right)^{\frac{1}{3}} \]

\[ C_{2c} = \left( \frac{Y_{Xe} F \sqrt{k_{11}}}{3\sqrt{2bk_{11}k_{12}}} \right)^{\frac{2}{3}} \]

Problem 13.3

13.8.2 Heterogeneous Nucleation

Speculation about the effect of fission fragment path length and nucleation on dislocations.
13.9 Growth of Stationary Bubbles

Assumptions

1.) After $t_c$, the bubble density is constant, they only change in size.

2.) Neglect directed motion.

3.) Use growth only by single vacancies or gas atoms.

4.) Assume all bubbles the same radius at the start.

*5.) No gas in the matrix, all in bubbles.

*6.) Resolution neglected.

*7.) Bubbles are in mechanical equilibrium.

8.) Either perfect or Van der Waal’s gas law is applicable.

13.9.1 Simplest growth model

Condition 5 yields;

$$ Y_{xe} \sum F t = mN $$

show;  

$$ R = \sqrt{\frac{3kTY_{xe} \sum F t}{4\pi 2\gamma N}} $$
and;
\[
\frac{\Delta V}{V} = \sqrt{\frac{3}{4 \pi N}} \sum \left( \frac{kT}{2 \gamma} \right)^{\frac{3}{2}} \sum \left( Y_{Xe} \sum F t \right)^{\frac{3}{2}}
\]

**13.9.2 Allowance for Gas Remaining in the Matrix**

Finds that allowance for some gas to remain in the matrix can reduce swelling by a factor of 10 at low temperatures, but there is very little effect at \( T > 1000 - 1500 \, ^{\circ}K \)

**13.9.3 Bubble Growth with Resolution**

Starting with;
\[
\frac{dC}{dt} = Y_{Xe} \sum F - 2k_{11}C^2 - \left( \sum_{m=2}^{\infty} k_{lm}C_m \right)C + 2C_2b + \left( \sum_{m=2}^{\infty} mC_m \right)b
\]

can neglect in growth stage

--------

After much manipulation;
\[
\frac{1 - f_b}{2} = \frac{b}{f_b^3} = \frac{4 \pi N}{3} D_{Xe} \left( 3BY_{Xe} \sum F t \right)^{\frac{2}{3}}
\]

Where \( f_b = \text{fraction of gas in bubbles} \)

Figure 13.15
Fig. 13.15  The effect of re-solution on bubble growth in the quasi-stationary approximation.
Resolutioning important at high fission rates and low temperature.

Figure 13.16

13.9.4 Growth of non Equilibrium Bubbles

We normally assume the bubble can attract all the vacancies it needs to retrain mechanical equilibrium. But as the bubble gets bigger, it needs more vacancies:

\[
\frac{(m_v)_{eq}}{m_{gas}} = \left(\frac{kT}{2\gamma}\right) \frac{R}{\Omega} + \frac{B}{\Omega}
\]

<table>
<thead>
<tr>
<th>( R ) Å</th>
<th>( \frac{(m_v)<em>{eq}}{m</em>{gas}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>1000</td>
<td>27</td>
</tr>
</tbody>
</table>

Orlander next sets up vacancy and interstitial equations to get growth.

(solves for \( C_V \) and \( C_i \))

Figures 13.17 a & b
Olander finds that growth rate is;
\[
\frac{dR}{dt} = \frac{\Omega}{R} \left[ D_v \left( 1 - \frac{Z_v}{Z_i} \right) (C_v - C_v^{eq}) + \frac{\Omega}{kT} \left( p - \frac{2\gamma}{r} \right) (D_v C_v^{eq} + D_i C_i^{eq}) \right]
\]

Effect of supersaturation
Effect of pressure on growth imbalance
.. \( p > \frac{2\gamma}{r} \)

**Chemical stress term**

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**13.9.5 Bubble Size Distribution During Growth**

*Read for general information* (Problem 13.9)
Fig. 13.16 Effect of re-solution on gas precipitation during irradiation: $\dot{F} = 4 \times 10^{13}$ cm$^{-3}$ sec$^{-1}$; $b = 5 \times 10^{-5}$ sec$^{-1}$; and $N = 2 \times 10^{17}$ cm$^{-3}$.
Fig. 13.17 Steady-state point-defect concentrations in an irradiated solid. ——, high defect production rate; ----, low defect production rate. The upper and lower curves for each defect production rate represent small and large dislocation densities, respectively. [After H. Wiedersich, Radiat. Eff., 12: 111 (1972).]