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.

$$m = \left(\frac{4\pi R^3}{3}\right) \bullet \left(\frac{2\gamma}{RkT}\right)$$

$$\frac{m_f}{m_o} = \frac{R_f^2}{R_0^2}$$

$$\frac{\left(\Delta V/V\right)_f}{\left(\Delta V/V\right)_0} = \frac{\left(\frac{4\pi R_f^3}{3}\right)}{\left(\frac{4\pi R_0^3}{3}\right)} \bullet \left(\frac{N/2}{N}\right)$$

$$\frac{\left(\Delta V/V\right)_f}{\left(\Delta V/V\right)_0} = 2^{\frac{3}{2}}\, x\, \frac{1}{2} = \sqrt{2}$$

Analysis of bubble coalescence in the <u>Absence</u> 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 = #of bubbles containing m gas atoms

b.) If we allow all bubbles to move;

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

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

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

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

Rate Constant

$$k_{ij} = 4\pi\left(R_i + R_j\right) \bullet \left(D_{bi} + D_{bj}\right)$$

$$Rate = 4\pi\left(R_i + R_j\right) \bullet \left(D_{bi} + D_{bj}\right)\left\{1 + \frac{\left(R_i + R_j\right)}{\sqrt{\pi\left(D_{bi} + D_{bj}\right)t}}\right\}C_i C_j$$

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;

$$= \pi\left(R_i + R_j\right)^2\left(v_{bi} - v_{bj}\right)C_i$$

But since there are $C_j \ \frac{\text{bubbles}}{\text{cm}^3}$ **;**

$$k_{ij} = \pi\left(R_i + R_j\right)^2\left(v_{bi} - v_{bj}\right)$$

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

Figure 13.11

$$\frac{\text{Gas bubbles destroyed}}{\text{cm}^3\text{-sec}} = b'C_m$$

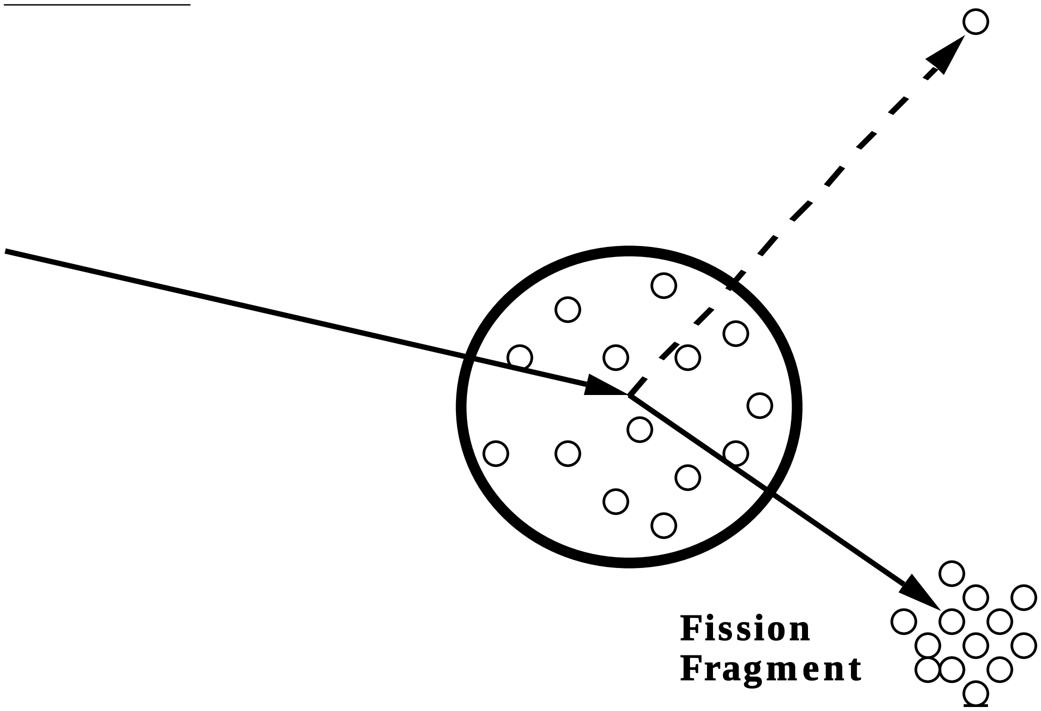
b' = prob./s that a bubble in fuel is destroyed.

$$= 2\pi R^2 \mu_{ff} \dot{F}$$

gas atoms returned to the matrix from bubble per cm^3 and per second. = b'm N

bubbles/cm^3 which contain m gas atoms

<u>Nelson</u>



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

\f(gas atoms returned to matrix from bubbles,cm^3 sec)

= bmN

Where

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

----

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 ≈ 30 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

$$\frac{dC}{dt} = Y_{Xe}\dot{F} - 2k_{11}C^2 - k_{12}CC_2$$

Fission--> g

Conc. of single gas atoms	**2 consumed per diatomic**	**Triatomic**

g +g <==>g$_2$

g +g$_2$<=> g$_3$

$$-k_{1m}CC_m + 2(2C_2)b + \ldots + mC_mb$$

....

g + g$_m$<=> g$_{m+1}$

Assumes whole bubble dissolved

note; only simple gas atoms added, not clusters.
For diatomic clusters

$$\frac{dC_2}{dt} = k_{11}C^2 - k_{12}CC_2 - (2C_2)b + (3C_3)b + \ldots.$$

in general,

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

Balence on gas atoms;

$$Y_{Xe}\dot{F} = \frac{dC}{dt} + 2\frac{dC_2}{dt} + \ldots.. + m\frac{dC_m}{dt}$$

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

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

Growth by addition **Resolution**

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

Figure 13.13

at high temperatures and low fission rates;

$$C_c = \sqrt{\frac{Y_{Xe}\,\dot{F}}{3k_{11}}}$$

$$C_{2c} = \sqrt{\frac{Y_{Xe}\,\dot{F}\,k_{11}}{3k_{12}^{2}}}$$

at low temperatures and high fission rates;

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

$$C_{2c} = \left(\frac{Y_{Xe}\,\dot{F}\,\sqrt{k_{11}}}{3\sqrt{2b}\,k_{11}k_{12}}\right)^{\frac{2}{3}}$$

Problem 13.3

<u>13.8.2</u> <u>Heterogeneous</u> <u>Nucleation</u>

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;

$$Y_{Xe}\dot{F}t = mN$$

show; $$R = \sqrt{\frac{3kTY_{Xe}\dot{F}t}{4\pi 2\gamma N}}$$

and;

$$\frac{\Delta V}{V} = \sqrt{\frac{3}{4\pi N}} \bullet \left(\frac{kT}{2\gamma}\right)^{\frac{3}{2}} \bullet \left(Y_{Xe}\dot{F}t\right)^{\frac{3}{2}}$$

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 °K

13.9.3 Bubble Growth with Resolution

Starting with;

$$\frac{dC}{dt} = Y_{Xe}\dot{F} - 2k_{11}C^2 - \left(\sum_{m=2}^{\infty} k_{lm}C_m\right)C + 2C_2 b + \left(\sum_{m=2}^{\infty} mC_m\right)b$$

can neglect in growth stage

After much manipulation;

$$\frac{(1 - f_b)}{f_b^{\frac{2}{3}}} = \frac{b}{(4\pi N)^{\frac{2}{3}} D_{Xe} \left(3 B Y_{Xe} \dot{F} t\right)^{\frac{2}{3}}}$$

Where f_b = fraction of gas in bubbles

Figure 13.15

Resolutioning important at high fission rates and low temperature.

Figure 13.16

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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 ;

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

R Å	$\frac{(m_v)_{eq}}{m_{gas}}$
10	2

100	6
1000	27

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;

$$\frac{dR}{dt} = \frac{\Omega}{R}\left[D_v\left(1 - \frac{Z_v}{Z_i}\right)\left(C_v - C_v^{eq}\right) + \frac{\Omega}{kT}\left(p - \frac{2\gamma}{r}\right)\left(D_v C_V^{eq} + D_i C_i^{eq}\right)\right]$$

effect of supersaturation on growth

Effect of pressure imbalance .. p > $2\gamma/r$

Chemical stress term

<u>13.9.5 Bubble Size Distribution During Growth</u>

Read for general information
(Problem 13.9)

Problem 13.4

Assume only 2 groups of bubbles in fuel

r_1 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 $= \frac{4}{3}\pi n\left(r_1^3 + r_2^3\right)$

n= 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:

$$N_i = p_i\left(\frac{4\pi r_i^3}{3kT}\right) = \frac{4\pi}{3}\left(\frac{2\gamma}{kT}\right)r_i^2 \qquad i=1,2$$

We have 3 types of collisions;

I + I
I + II
II + I
II + II

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:

$\frac{n}{4}$ bubbles of type I + I

$\frac{n}{4}$ bubbles of type II + II

$\frac{n}{2}$ bubbles of type I + II, II +I

=======================================

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

$$p = \frac{2\gamma}{r}$$

$$p\left(\frac{4\pi r^{3}}{3}\right) = NkT$$

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

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

Final volume of gas

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

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

$$V_{initial} = \frac{4\pi n}{3}\left(r_1^3 + r_2^3\right)$$

$$Swelling = \frac{\frac{1}{\sqrt{2}}\left(r_1^3 + r_2^3\right) + \frac{1}{2}\left(r_1^2 + r_2^2\right)^{\frac{3}{2}}}{\left(r_1^3 + r_2^3\right)} - 1$$

but $r_2 = 0.5\ r_1$

$$\frac{\Delta V}{V} = \frac{1}{\sqrt{2}} + \frac{\frac{r_2^3}{2}\left(1 + 4\right)^{\frac{3}{2}}}{r_2^3\left(1 + 8\right)} - 1 = 0.328$$

Problem 13.5

What is the Effect of Irradiation on Diffusion ?

Self diffusion in U metal by vacancies

$$D_U = x_v a_o^2 \nu \exp\left(-\frac{\varepsilon_v^*}{kT}\right)$$

frac. of vac. *migration energy of vacancies*

a.) What is D_U in absence of irradiation?

b.) What is the vacancy fraction for a fission rate of $\dot{F}$ when Y_{vi} pairs of defects are produced per FF?

c.) What is the diffusivity in that radiation field?

d.) If the energy of motion for interstitials is ε_i^*, sketch the temperature dependence of D_U.

----

a.) When there is no irradiation;

$$x_v = x_v^{eq} = \exp\left(-\frac{\varepsilon_v}{kT}\right)$$

Where E_v is formation energy of vacancies

$$D_U^{th} = a_o^2 \nu \exp -\left(\varepsilon_v^* + \varepsilon_v\right)$$

b.) When recombination is the only means of

destruction, then the equilibrium between production and destruction rates gives (see eqs. 13.186, 13.187)

$$Y_{vi}\dot{F} = k_{iv} C_v C_i \qquad (1)$$

it is assumed that

But, to a first approximation,

$$C_v = C_i$$

$$\text{and, } C_v = x_v \left(\frac{x_v}{\Omega}\right) = \frac{x_v}{a_o^3}$$

so, using 1.)

$$x_v = a_o^3 \sqrt{\frac{Y_{vi}\dot{F}}{k_{iv}}}$$

$$k_{iv} = \frac{Z_{iv}\Omega D_i}{a_o^2} = Z_{iv} a_o D_i$$

c.) The recombination rate is (eq. 13.42)

$$k_{iv} = \frac{Z_{iv}\Omega D_i}{a_o^2} = Z_{iv} a_o D_i$$

substituting into expression for x_v

$$x_v = a_o^3 \sqrt{\frac{Y_{vi}\dot{F}}{Z_{iv} a_o D_i}}$$

and replacing x_v^{eq} with x_v above

$$D_V^{rad} = a_o^2 \nu \left\{ a_o^3 \sqrt{\frac{Y_{vi}\dot{F}}{Z_{vi} a_o D_i}} \right\} \mathbf{exp}\left(-\frac{\varepsilon_v^*}{kT} \right)$$

But since $D_i = a_o^2 \nu \ \mathbf{exp}\left(-\frac{\varepsilon_i^*}{kT} \right)$

$$D_v = \sqrt{\frac{a_o^7 Y_{iv} \dot{F} \nu}{Z_{iv}}} \left(\mathbf{exp} \frac{\left[\frac{\varepsilon_i^*}{2} - \varepsilon_v^* \right]}{kT} \right)$$

Problem 13.8

Calculate the average chord length of a parallel beam of fission fragments impinging on a bubble of radius R

ρ = *track length for impact parameter b*

= *chord length through circle*

= $2R \sin \theta$

$$= 2R\sqrt{\left[1-\left(\frac{b}{R}\right)^2\right]}$$

Let p(b) db = probability of a FF striking with an impact parameter in (b, db)

(i.e., if it indeed does strike the bubble)

$$p(b)db = \frac{2\pi b\,db}{\pi R^2} = \frac{2b\,db}{R^2}$$

since;

$$\int_0^R p(b)\,db = 1$$

and

$$\bar{\rho} = \int_0^R p(b)\rho(b)\,db = \int_0^R \left(\frac{2b}{R^2}\right)\left(2R\sqrt{1-\left(\frac{b}{R}\right)^2}\right)db$$

$$\bar{\rho} = 4R\int_0^R \left(\sqrt{1-\left(\frac{b}{R}\right)^2}\right)\frac{b}{R^2}\,db$$

let $\eta = b/R$

$$\bar{\rho} = 4R\int_0^1 \sqrt{1-\eta^2}\bullet \eta\, d\eta$$

if $\omega = \eta^2$**,** $d\omega = 2\eta\, d\eta$

$$\frac{\bar{\rho}}{R} = 2\int_0^1 \sqrt{1-\omega}\bullet d\omega$$

$$= 2\left[-\frac{2}{3}(1-\omega)^{\frac{3}{2}}\right]_0^1$$

$$\bar{\rho} = \frac{4}{3}R$$