13.10 Migration Mechanisms and Growth of Mobile Bubbles

• Now we let bubbles move too.
  • Distinguish between as fabricated (some He) and equilibrium (Xe filled) bubbles

13.10.1. Atomic Mechanism of Bubble Mobility Due to Surface Diffusion

Remember, surface atoms are in constant motion, the slightest imbalance can cause bubbles to move.

13.10.2 Random Bubble Motion

There are two diffusivities of major importance

• Surface Diffusivity ($D_s$)
• Bubble Diffusivity ($D_b$)

In chapter 7;

$$D_s = \frac{\lambda_s^2 \Gamma_s}{4} \quad (2 \text{ dimensional})$$

**total jump frequency of molecules on surface**

$$D_b = \frac{\lambda_b^2 \Gamma_b}{6} \quad (3 \text{ dimensional})$$

**jump frequency of bubble**
To relate $\lambda_s$ to $\lambda_b$, note that from the cube model of figure 13.18

$$\lambda_b = \frac{\text{distance that bubble moves}}{\# \text{ of jumps to move bubble } \Delta x} = \frac{\Delta x}{l^3 \Delta x} = \frac{\Omega \lambda_s}{l^3}$$

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For a spherical bubble;

$$\lambda_b = \left( \frac{\frac{a_o^3}{4\pi R^3}}{\frac{4\pi R^3}{3}} \right) \lambda_s$$

Since # of surface atoms $= \left( \frac{4\pi R^2}{a_o^2} \right)$

Frequency of bubble jumps;

$$\Gamma_b = \left( \frac{4\pi R^2}{a_o^2} \right) \Gamma_s$$

This gives;

$$D_b = \frac{3a_o^4 D_s}{2\pi R^4}$$
Fig. 13.18 Diagram for determining the jump distance of a bubble due to individual jumps of molecules on its inner surface.
or;

\[ D_b = \left[ \frac{3a_o^4 D_{so}}{2\pi} \exp \left\{ -\left( \frac{E_s}{kT} \right) \right\} \right] \cdot \left( \frac{1}{R^4} \right) \]

Small bubbles move faster than large ones

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13.10.3 Directed Bubble Migration in a Temperature Gradient

Introduction of bubble disturbs temperature profile (see figure 13.19)

One finds that;

\[ \left( \frac{dT}{dx} \right)_b > \left( \frac{dT}{dx} \right)_{\text{normal}} \]

or;

\[ \left( \frac{dT}{dx} \right)_b = \frac{3}{2} \left( \frac{dT}{dx} \right) \]

Note that the flux of atoms along surfaces (chapter 7) is;

\[ J_s = \left( -\frac{D_s Q_s^* C_s}{kT^2} \right) \cdot \left( \frac{dT}{dx} \right)_b \]

and;

\[ v_b = \left( -\frac{3D_s Q_s^* a_o}{kT^2 R} \right) \cdot \left( \frac{dT}{dx} \right) \]

Note \( Q_s^* \) (heat of transport) must be positive because bubbles move up a temperature
Fig. 13.19 Bubble migration in a temperature gradient. (a) Flow of surface molecules across faces parallel to the temperature gradient. (b) Temperature profiles in the solid and through the bubble.
Olander calculates for:
\[ R = 100 \, \text{Å} \quad a_0 = 3 \, \text{Å} \quad T = 1000^\circ \text{K} \]
\[ Q_s^* = 415 \, \frac{kJ}{\text{mole}} \quad \frac{dT}{dx} = 4000 \, \frac{^\circ \text{K}}{\text{cm}} \]
\[ D_s = 5 \times 10^{-7} \, \frac{\text{cm}^2}{\text{sec}} \]
gives:
\[ \nu_b = 3 \times 10^{-6} \, \frac{\text{cm}}{\text{sec}}, \quad 0.2592 \, \frac{\text{cm}}{\text{day}}, \quad 1.814 \, \frac{\text{cm}}{\text{week}} \]

But \( T \) changes with time, so we cannot extrapolate too long.

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13.10.4 General Treatment of Bubble Mobility

Fred Nicols (now at ANL) has been a major contributor in this area.

\[ \nu_b = \text{mobility} \times \text{force} = M_b F_b = \frac{D_b F_b}{kT} \]

Nicols relates macroscopic and microscopic forces to find:

\[
F_b = \left( \frac{2\pi R^3}{a_0^3} \right) \left( \frac{Q_s^*}{T} \right) \left( \frac{dT}{dx} \right)
\]
13.10.5 Bubble Migration by Volume Diffusion

Consider the effect of vacancy motion outside the bubble. Need to get new expressions for bubble jump frequency and jump distance. 

\{See Figure 13.20\}

Assuming that a bubble is a perfectly absorbing sphere;

\[ \Gamma_b = \frac{4\pi R^2 D_{vol}}{a_o^4} \]
\[ \lambda_b = \left( \frac{3a_o^3}{4\pi R^3} \right) \cdot \sqrt{\frac{\lambda_v^2}{R}} \]

Problem of determining this distance has been treated by Olander

\[ \bar{\lambda}_v^2 = 2Ra_o \]

Remember that

\[ D_b = \frac{\lambda_b^2 \Gamma_b}{6} \]

Which produces (for Brownian motion);

\[ D_b = \left( \frac{3a_o^3}{4\pi} \right) \left( \frac{1}{R^3} \right) D_{vol} \]

For surface diffusion \( D_b \propto \frac{1}{R^4} \) Have to get for moving species
Fig. 13.20 Typical trajectory of a vacancy emitted from, then recaptured by, the bubble. The random walk is assumed to start from point P.
Next, consider the effect of a temperature gradient;

\[ v_b = \frac{D_b F_b}{kT} \]

where \[ F_v = -\left( \frac{Q_v^*}{T} \right) \cdot \left( \frac{dT}{dx} \right)_b \]

and \[ Q_v^* = \text{heat of vacancy transport} \approx \text{energy of self diffusion} \]

Nicols finds;

\[ v_b = \left( \frac{D_{vol} Q_v^*}{kT^2} \right) \cdot \left( \frac{dT}{dx} \right) \]

Problem 13.2
13.10.6 Bubble Migration in a Stress Gradient

Trick is to calculate the force on a bubble as it moves from $x$ to $x + dx$ and the stress changes from $\sigma$ to $\sigma + d\sigma$.

$$F_b = -\frac{dG_b}{dx} \quad \text{(at constant temp.)}$$

Gibbs free energy of bubble

Three contributions to $G_b$:

1.) Change in free energy of contained gas, $dG_g$

2.) Change in free energy of system due to change in surface area, $dG_s$

3.) Change in strain energy of solid, $dE_{\text{solid}}$

For an Ideal Gas;

$$dG_b = -p \, dV = -p(4 \pi R^2 dR)$$

For surface energy;

$$dG_s = \gamma (8\pi R dR)$$
or, \[ dG_g + dG_s = -4\pi R^2 \left\{ p - \left( \frac{2\gamma}{R} \right) \right\} dR \]
since \( p - \left( \frac{2\gamma}{R} \right) = \sigma \)

Need to get this in terms of \( x \)

Use;

\[ \left( \sigma + \left[ \frac{2\gamma}{R} \right] \right) \cdot \left( \frac{4\pi R^2}{3} \right) = mkT \]

differentiating;

\[ \frac{dR}{d\sigma} = -\left( \frac{R^2}{3\sigma R + 4\gamma} \right) \]

but,

\[ dR = \left( \frac{dR}{d\sigma} \right) \cdot \left( \frac{d\sigma}{dx} \right) dx \]

So;

\[ dR = -\left( \frac{R^2}{3\sigma R + 4\gamma} \right) \cdot \left( \frac{d\sigma}{dx} \right) dx \]

This gives;

\[ \left( \frac{dG_g}{dx} \right) + \left( \frac{dG_s}{dx} \right) = \left\{ \frac{4\pi R^4 \sigma}{3\sigma R + 4\gamma} \right\} \left( \frac{d\sigma}{dx} \right) \]

For elastic energy, start with

\[ E_{el} = \frac{\sigma^2}{2K} \quad \text{Bulk Modulus} \]
and end up with;

\[
\frac{dE_{\text{solid}}}{dx} = - \left[ \frac{2\pi \sigma R^3}{3K} \right] \cdot \left\{ \frac{3\sigma R + 8\gamma}{3\sigma R + 4\gamma} \right\} \cdot \left( \frac{d\sigma}{dx} \right)
\]

Put it all together;

\[
F_b = - \left\{ \frac{4\pi R^2\sigma}{3\sigma R + 4\gamma} \right\} \cdot \left[ 1 - \left( \frac{3\sigma R + 8\gamma}{6RK} \right) \right] \cdot \left( \frac{d\sigma}{dx} \right)
\]

For small bubbles and low \(\sigma\) and large stresses;

\[
F_b = -\left( \frac{\pi R^4\sigma}{\gamma} \right) \cdot \left( \frac{d\sigma}{dx} \right)
\]

For large bubbles and high stresses;

\[
F_b = -\left( \frac{4\pi R^3}{3} \right) \cdot \left( \frac{d\sigma}{dx} \right)
\]

Bubbles always move down a stress gradient!

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\[
\frac{(F_b)_{\text{stress}}}{(F_b)_{\text{temp}}} = \frac{(R\sigma^2 a_o^3)}{2\gamma kT \left[ \frac{Q^* \sigma}{kT} \right]} \cdot \frac{\left( \frac{1}{\sigma} \right)}{\left( \frac{d\sigma}{dx} \right)} \cdot \frac{1}{T} \frac{dT}{dx} \approx 0.01
\]
Problem 13.2

a.) What is the root mean squared distance traveled in 40 days by a 20 Å diameter bubble undergoing Brownian motion in UO₂ at 1400 °C

b.) Recalculate a.) in a temperature gradient of 2000 °C/cm

Assume that the bubble diffusivity is governed by surface diffusion and \( Q_s^* = 415 \) kJ/mole

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a.) From Ch. 7

\[
\begin{align*}
    r^2 &= 6D_b t = \frac{9a_0^4 D_s t}{\pi R^4} \\
    \text{eq. 13.214} \\
    \text{use } a_0 &= 3 \text{ Å} \\
    t &= 40 \cdot 24 \cdot 3600 = 3.46 \times 10^6 \text{ s} \\
    R &= 10 \text{ Å} \\
    T &= 1400 \text{ °C} = 1673 \text{ °K} \\
    \text{eq. 13.216} \\
    D_s &= 4 \times 10^5 \cdot \exp (-108/RT) \text{ cm}^2/\text{s}
\end{align*}
\]
\[ \sqrt{r^2} = \left( \frac{9 \cdot 3^4 \cdot 2.77 \times 10^{-9} \cdot 3.46 \times 10^6}{\pi \cdot 10^4} \right)^{\frac{1}{2}} \]

\[ = 0.015 \text{ cm} \]

b.) Thermal Gradient Migration

**eq 13.219**

\[ r = \left( \frac{3D_s Q_s^* a_o}{RkT^2} \right) \cdot \left( \frac{dT}{dx} \right)_t \]

\[ r = \left( \frac{3 \cdot 2.77 \times 10^{-9} \cdot 100 \times 10^3 \cdot 4.18 \cdot 3 \cdot 2000 \cdot 3.46 \cdot 10^6}{10 \cdot 1.38 \times 10^{-23} \left( \frac{J}{\circ K} \right)[1673]^2 \cdot 6.02 \times 10^{23}} \right) \]

\[ = 0.310 \text{ cm} \]

In other words, the bubble moves almost 21 times farther in a temperature gradient.