Lecture Notes from Monday 04/20/202

Hi-Temp

## Topics

    (i)   Deformation mechanism
    (ii)   Diffusion Mechanism
    (iii)   Description of diffusion: Coefficient of Diffusion
    (iv)   Flux of diffusing atoms in response to a driving force
    (v)   The gradient of the chemical potential under a uniaxial stress as the driving force
   (vi)   Derivation of the strain-rate for mass transport by boundary diffusion.

(i) The Deformation Mechanism

In the last lecture we discussed how a small crystallite can change its shape under uniaxial load, by the moving atoms from one crystal face to the orthogonal face. We calculated the strain in terms of the number of atoms transported and the grain size (equal to the volume of mass divided by d^3, where d is the grain size).

The above topic was considered in a "free" single crystal, that is one with open surfaces. But we showed that the ledge structure of grain boundaries allows them act like surfaces since they atoms can be added to etched from the ledges allowing the crystallite, surrounded by other crystallite, to change shape in the same manner as a free crystal.


Bndry A - atoms flow out

B

A

grains move towards each other as rigid bodiesa

δ_{gb}

δ_{gb}
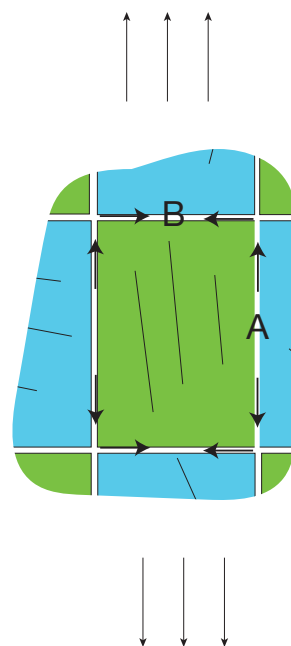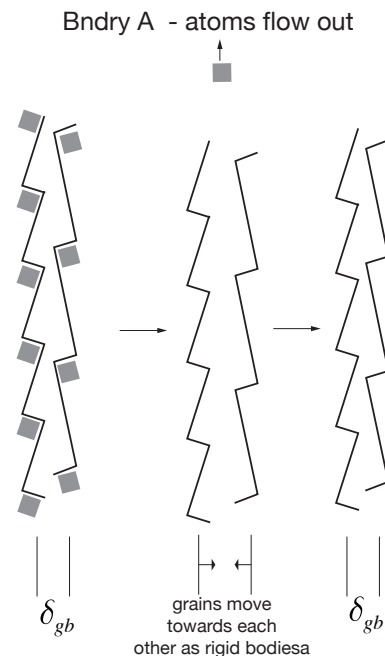
δ_{gb} = effective width of the boundary

Bndry B - atoms flow in

The schematic shown just above further expands on the above concept. On the left a tensile stress is applied to a polycrystal in the vertical direction. The deformation of the polycrystal is fully captured in the deformation of one crystal shown in green color, just above. Note that a tensile stress is applied across boundary B, but not across A. This bias causes atoms to be removed from A and plated into B; the arrows in the figures show the path of mass transport.

The right hand figure illustrates how removing the atoms from boundary A (the atoms being removed as marked by shaded squares) is accommodated by the two crystal moving together as rigid body; this displacement leads to transverse strain. By equivalence the atoms deposited on boundary B, also at ledged will cause the two crystals to move outwards leading to tensile strain in the uniaxial direction.

(ii) The Diffusion Mechanism

For atoms to be transported from A to B, they have to "diffuse" through the boundary. There not enough space in the boundary width, written as δ_{gb} , for the atoms to move will ease. They have to climb over the hurdles, or narrow spaced as illustrated in the upper figure just below.
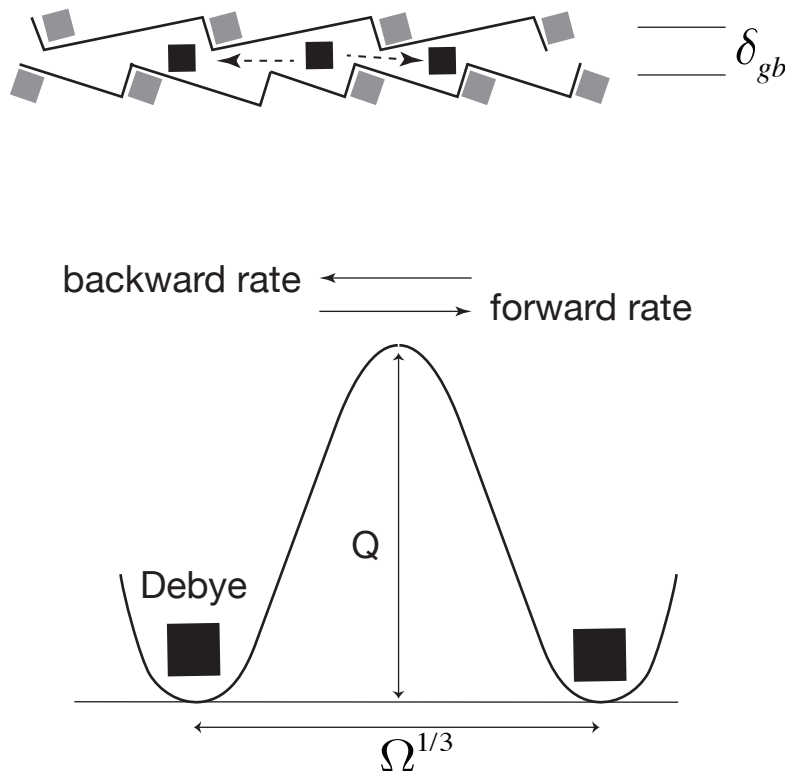
The mechanism of diffusion is illustrated in the figure just above. This figure refers to random motion of the atoms in either direction, which is appropriate to describe the fundamental diffusion mechanism. Note that the atom moves in jumps, over a distance of about the interatomic spacing, $\Omega^{1/3}$. In this instance there is no preferred direction for atom movement, therefore, the forward and the backward rate of jumps is equal.

(iii) A General Description of the Coefficient of Diffusion

We note that the atoms must move in jumps, where each jump involves an energy barrier (a hill), as illustrated in the lower figure. What happens is that the atom sitting in a comfortable energy well vibrates at a frequency known at the Debye frequency (it is approximately 10^{13} s^{-1}). Now an then it jumps over the energy barrier. Therefore, the rate of jumps are given by the product of the Debye frequency, υ_D, multiplied by the probability of jump

$$\text{Rate of jumps} = \upsilon_D e^{-\frac{Q}{RT}} \quad \text{\#jumps per second} \tag{1}$$

D is the diffusion coefficient, equal to the jump distance squared divided by 6 (six directions of possibility for jumps), multiplied by the jump rate.

The "activation barrier", is specified by the activation energy, Q (J mol^{-1}) while RT, the thermal energy is a product of the gas constant (J mol^{-1}K^{-1}) and temperature (K). The units for these parameters are enclosed within the brackets. Note that Q/RT is a dimensionless quantity (as is must be since the exponential can be expanded as a power series).

Now, the diffusion of atoms along the boundary can be shown to be given by the diffusion coefficient

$$D = \frac{\Omega^{2/3}}{6} \upsilon_D e^{-\frac{Q}{RT}} \tag{2}$$

The diffusion coefficient is the product of the *square* of the jump distance, taken here to be the interatomic spacing $\Omega^{1/3}$, multiplied by the rate of jumps. Thus D has units of m^{2}s^{-1}. The factor of 6 in the denominator appears because the atoms can jump in any of six possible directions (for diffusion in three dimensions), only one of which is in a specific direction.

Eq. (2) is phenomenologically written as following

$$D = D_o e^{-\frac{Q}{RT}} \tag{3}$$

D_o is called the preexponential, it has units of m^{2}s^{-1}.

In the present analysis we are concerned with diffusion along the grain boundary (diffusion can also occur through the lattice which we shall consider later). For this special case we write Eq. (3) with the following notation

$$D_{gb} = D_{gb}^o e^{-\frac{Q_{gb}}{RT}} \tag{4}$$

Thus the pre-exponential and the activation energy are now specific to boundary diffusion.

Data for the diffusion coefficients for many different materials are found at the following link

H. J. Frost "Deformation Mechanism Maps"
https://engineering.dartmouth.edu/defmech/

(iv) Flux of Diffusing Atoms Under a Driving Force

In the above section we considered random motion of atoms by diffusion. However under a driving force for the atoms to move in a specific direction, the jumps in the forward and backward direction are unequal giving rise to a preferred direction of diffusional flux. We specify this driving force as a gradient in the chemical potential ($\Delta\mu$) of atoms. The mechanism of this directional diffusion is described by the schematic shown below
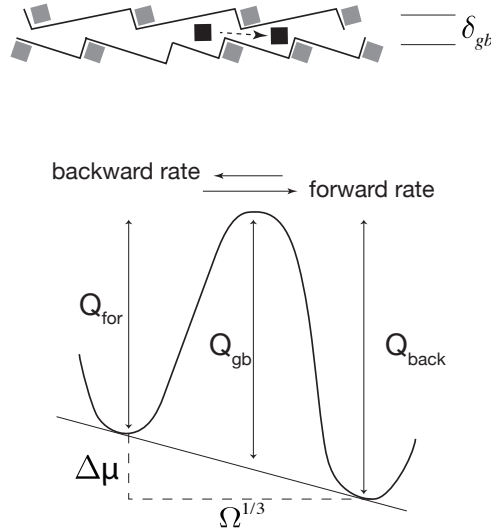
Please note the following points regarding the above schematic

(i) The driving force for individual atoms jumps, $\Delta\mu$, causes the activation barrier for the forward jumps, Q_{for}, to become lower than for the backward jumps, Q_{back}. Since the mean value of the activation barrier is still Q_{gb}, it is clear that

$$Q_{for} = Q_{gb} - \frac{\Delta\mu}{2}$$

And that

$$Q_{back} = Q_{gb} + \frac{\Delta\mu}{2}$$

Therefore the net probability of forward jumps will be given by

Net forward jump probability $= e^{-\frac{Q_{gb}-\frac{\Delta\mu}{2}}{RT}} - e^{-\frac{Q_{gb}+\frac{\Delta\mu}{2}}{RT}} = e^{-\frac{Q_{gb}}{RT}}\left(e^{\frac{\Delta\mu}{2RT}} - e^{-\frac{\Delta\mu}{2RT}}\right)$.

Expanding the terms in the brackets in polynomial form and taking the first term as a good approximation since usually $\frac{\Delta\mu}{2RT} \ll 1$, we obtain

Net forward jump probability $= \frac{\Delta\mu}{k_B T} e^{-\frac{Q_{gb}}{RT}}$ (5)

where we have replaced R by k_B since we wish to represent the equation on a per atom rather then a per mole basis (the Gas Constant is based on per mole). Note that the pre-exponential in Eq.(5) is dimensionless.

The driving force for diffusion flux (in a specific direction) is related to the driving force, that is, the gradient of the chemical potential in that direction. For the problem as hand the driving force which we now write a a gradient of the chemical potential is them given by

$$\frac{d\Delta\mu}{dx} = \frac{\Delta\mu}{\Omega^{1/3}} \qquad (6)$$

The flux equation for diffusion under a driving force (for the present case of grain boundary diffusion) is given by

$$J = \frac{D_{gb}}{\Omega k_B T}\frac{d\Delta\mu}{dx} \qquad (7)$$

Let us check the units in the above equation

J #atoms m^{-2} s^{-1}

D_{gb} m^{2}s^{-1}

Ω m^{3}atom^{-1} (that is volume per atom)

$k_B T$ thermal energy per atom, in J atom^{-1}

$\Delta\mu$ Chemical potential of the species, i.e. energy pre atom, in J atom^{-1}

" dx "   m (distance)

The units are consistent. Note that atom is also treated as a unit (same as mole divided by the Avogadro's number)

Equation (7) can be used to derive an equation for the strain rate as a function of temperature, applied stress and the grain size, as done in the next lecture. First we need to show how the difference in the chemical potential is related to the applied stress.

(v) The gradient of the chemical potential under a uniaxial stress as the driving force
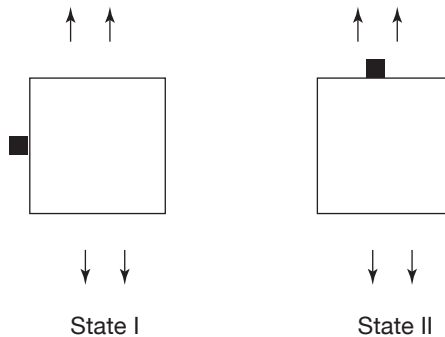
State I   State II

The difference in the Gibbs Free energy of the two states is equal to the difference in between the chemical potential of the atom in State II where it is subjected to a tensile traction, and in State I where it is traction free. The difference in the Gibbs Free energy is equal to work that the

system can do on the environment in moving from State I to State II. The work is negative since the system does work on the surroundings. Therefor

$$\Delta\mu = -(\sigma\Omega^{2/3})\Omega^{1/3} \qquad\qquad (8)$$

The work done is equal to the force exerted on the atom which is equal to the stress multiplied by the area of the atom, which is equal to $\Omega^{2/3}$, multiplied by the displacement which is equal to $\Omega^{1/3}$. Thus Eq. (8) reduces to the following simple result,

$$\Delta\mu = -\sigma\Omega \qquad\qquad (9)$$

Now going to the first figure in this lecture, the chemical potential for the atoms on boundary B is equal to $-\sigma\Omega$, while on the A boundary it is equal to zero, since the stress is absent.

The driving force for diffusion of atoms from A boundary to the B boundary is therefore approximately given by

$$\text{Driving force} = \frac{d\Delta\mu}{dx} = \frac{\Delta\mu}{d} = \frac{\sigma\Omega}{d} \qquad\qquad (10)$$

Where d on the right hand side is the grain size, while on the left it represents the derivative.

We are now ready to use Eq. (7) to obtain an equation for the strain rate as a function of "laboratory" variables, i.e. the temperature, the applied stress and the grain size.

(vi) Strain Rate by Boundary Diffusion

Nomenclature:

$\dot{V}$ the **rate** of the volume of atoms transported into the grain boundary associated with one grain

$\dot{N}$ is the rate of the number of atoms transported so that $\dot{V} = \Omega\dot{N}$

d is the grain size.. the surface area of one grain is d^2, and the strain associated with mass insertion (at one boundary of the grain) is the thickness of the plated layer divided by the grain size.

L is the effective diffusion distance from interface A to interface B

$\dfrac{d\Delta\mu}{dx}$ is the gradient of the chemical potential between boundary A and boundary B

σ the uniaxial tensile stress

Ω volume occupied in the crystal by one atom (think of cubes, each belonging to one atom) which are stacked together to form the crystal.

$k_B T$ the thermal energy per atom, where k_B is the Boltzmann's constant

T temperature in K

D_{gb} coefficient of grain boundary diffusion

δ_{gb} is the effective width of the boundary through which the atoms are transported

$\dot{\varepsilon}$ strain rate in units of s^{-1}

J is the diffusional flux of atoms in units of atoms cross-sectional-area^{-1} second^{-1}

$$\dot{\varepsilon} = \frac{\dot{V}}{d^2} \cdot \frac{1}{d}$$

The $\dot{V}$ will be the product of J, times the cross-section for transport, $d\delta_{gb}$, times the volume per atom.

$$\dot{V} = Jd\delta_{gb}\Omega$$

Thickness of the plated layer at boundary B, by dividing the volume deposited on one crystal face divided by the area of the crystal face

$$\Delta\dot{d} = 4\frac{\dot{V}}{d^2}$$

Therefore the strain rate

$$\dot{\varepsilon} = \frac{4d\delta_{gb}}{d^2} \cdot \frac{1}{d}\frac{D_{gb}}{k_B T}\frac{\sigma\Omega}{d}$$

(22.1) (April 22)

$$\dot{\varepsilon} = 4\frac{\sigma\Omega}{k_B T}\frac{\delta_{gb}D_{gb}}{d^3}$$

The above model can be tested in the laboratory since it relates the strain to experimental parameters, the stress, the temperature (through the diffusion coefficient) and the grain size.

(i) Measure the activation energy and compare with the general value for the activation energy for a given material (as in the Frost website). We do this by measuring the strain rate as a function of temperature at the same stress… and then make an Arrhenius plot to get Q_{gb}.

(ii) Note that the strain rate is directly proportional to the applied stress… this linear relationship is characteristic of viscous flow.

The viscosity from Eq. (Result) is now given by

$$\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{k_B T d^3}{4\Omega\delta_{gb}D_{gb}}$$

If we let $d = \Omega^{1/3}$ then we essentially have an amorphous structure and we are calculating the viscosity of such a material (fluids or silica)

$$\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{k_B T}{4\Omega^{1/3} D_{gb}}$$

The viscosity of fluids or amorphous materials is given by the Stokes Einstein equation is given by

$$\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{k_B T}{6\Omega^{1/3} D_{gb}}$$

The linear viscous relationship in diffusional creep bestows superplastic deformation properties to the polycrystal.

(iii) The strain is very sensitive to the grain size.. it is proportional to d^{-3}. So if the grain size can be reduced from 1 micrometer to 0.1 micrometer then the strain rate can be enhanced by three orders of magnitude.

Practice HW Problems

I. Write a one page essay (about 200 words) on what you have learnt about the relationship between diffusion of atoms in the solid state and high temperature deformation of polycrystals. You can write your answer as a sequence of points marked as (i), (ii), (iii) etc.

II. Give a short answer as to why the thickness of the layer deposited at a grain boundary depends only on the volume of the mass transported into it, and the grain size, so that it is independent of the density of the ledges in the grain boundary.

III. It is to be expected the Q_{gb} the activation energy for grain boundary diffusion is likely to be related to the enthalpy of melting of the crystalline material. Can you give an estimate for the ratio of these two quantities?

(iv) Please look at the website mentioned just after Eq. (4). Look up the activation energy for grain boundary diffusion for aluminum, and relate it to the heat of melting for this metal.

H. J. Frost "Deformation Mechanism Maps"
https://engineering.dartmouth.edu/defmech/