- Please attempt all questions and be concise in your answers.

- Time limit is 3 hours. You may use any hand-written notes you took in class, notes that I sent out, homework problems that you were assigned (and their solutions) but NO OTHER solutions and NO BOOKS. You may take one to two breaks.

- Please write things and draw diagrams clearly as it will improve quality and grades.
1. Consider diffusion of an atom which sits on top of a surface. The example we wish to examine is an atom sitting on top of a hexagonal plane of atoms, for example the (111) plane of an fcc crystal (Figure 4.7). Here the adatom is missing all of its nearest neighbors except the three atoms below. It moves around on the two-dimensional surface by diffusive hops.

![Figure 4.7: Schematic of (111) surface showing adatom (shaded) on preferred site.](image)

(a) Evaluate the relevant quantities for diffusion of this atom in the expression for diffusivity

\[ D = f(sa_0)^2 \nu pjz \]

Consider only the shortest possible hops between the three-fold coordinated sites on the surface. (On this surface the distance between nearest-neighbor atom centers is \( a/\sqrt{2} \), where \( a \) is the cubic lattice parameter. The shortest jump distance is \( a/\sqrt{6} \).)

(b) Based on your answer, would you expect the diffusivity of this atom on the surface to be greater or less than that of a bulk atom.

Now imagine that our surface has steps, which we assume are along the close-packed directions in the surface. When atoms moving around the surface impinge onto a step, either from above or below, they become incorporated into the step. Atoms incorporating into the step result in the step moving across the surface. The flux of atoms across the surface is given by

\[ J_s = -D \nabla c_s \]
Since the surface concentration $c_s$ is in atoms per area, the surface flux $J_s$ will be in atoms per length per time.

Figure 4.8: Schematic of diffusion of adatoms on surface showing flux to step.

(c) What is the relationship between the surface flux of atoms at the step and the step velocity? Consider the fluxes from both sides of the step.

Focus on the flux $J_+$ coming to the step from the left. It is often postulated that there is an anomalously large barrier associated with the atom hopping over the step edge. This is shown schematically as $\Delta G_s$ in Figure 4.9. Also when the atom has been incorporated into the step it has a lower energy by the amount $\Delta G_e$ relative to the free adatom, as also shown in Figure 4.9.

Figure 4.9: Schematic of atomic potential near step showing anomalous barrier height $\Delta G_s$ near step and edge binding energy $\Delta G_e$.

(d) Consider the relative rates of atoms hopping over the step from position 1 to position 2 and back from position 2 to position 1 in Figure 4.9. Calculate the net flux of atoms over the step. Use this to deduce the boundary condition for the top step region of the surface.
2. For the case of Zn impurities in Cu, calculate the interaction energy between a vacancy and the doubly-charged Zn impurity. Assume that the distance of closest approach is equal to the nearest-neighbor distance in Cu, and that $\alpha = 0.4$. Is this large enough to ensure that each Zn impurity will have a vacancy? Ignore the entropy of formation for vacancies and the vacancy-interstitial pair. The formation enthalpy for a vacancy in Cu is 1.29 eV.

3. For thin films, the stress state is often anisotropic, due to the biaxial constrain of the substrate and the free surface of the film. In his 1997 Applied Physics Letter (Vol. 70, p. 2810-2), Aziz points out that for anisotropic stress, we must consider the shape of the volume of forming a vacancy, i.e. we must consider the vacancy formation volume as a formation strain tensor. We consider the case of a thin film, where the predominant vacancy source or sink is the surface. Formation of a vacancy consists of removing an atom from the bulk and placing it on the surface, and then allowing the film to relax. The formation strain is then given by the sum of the two terms:

$$\Delta V_V = V_a \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} + \frac{\Delta V_r}{3} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

where the first term is the volume associated with creating a new lattice site on the surface, and the second term is the decrease in volume associated with relaxation around the vacancy.

For a film under the constraint of a substrate, the stress state is often equal-biaxial, given by

$$\sigma = \begin{bmatrix} \sigma_{11} & 0 \\ 0 & \sigma_{11} \end{bmatrix}$$

In this case the mechanical work done to create the vacancy is given by

$$W_V = -\sigma \cdot \Delta V_V = -\frac{2\sigma_{11}\Delta V_r}{3}$$
This is an energy term which must be incorporated into the vacancy formation energy, giving

$$\Delta G'_V(\sigma) = \Delta G'_V(0) - \sigma \cdot \Delta V_V$$

We wish to examine how important this can be for diffusion for a particular case of an epitaxial (111) oriented Pt film subject to a 0.8% compressive biaxial strain. The stress components for this strain state can be found from standard elasticity analysis. We find:

$$\sigma_{11} = M_b \epsilon_{11}$$

where $\epsilon_{11} = -0.008$, and $M_b$ is the biaxial modulus, which, for this case is given by:

$$M_b = \frac{6c_{44}(c_{11} + 2c_{12})}{c_{11} + 2c_{12} + 4c_{44}}$$

where $c_{ij}$'s are the components of the stiffness tensor, which for Pt are:

<table>
<thead>
<tr>
<th>ij</th>
<th>$c_{ij}$ (GPa)</th>
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<tbody>
<tr>
<td>11</td>
<td>347</td>
</tr>
<tr>
<td>44</td>
<td>76.5</td>
</tr>
<tr>
<td>12</td>
<td>251</td>
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Platinum is FCC with a lattice parameter of $a_0 = 3.924\text{Å}$. Assume that the magnitude of the volume of the vacancy is $\Delta V_V \approx 0.8V_A$, so that $\Delta V_\sigma \approx -0.2V_A$, where $V_A$ is the volume per atom.

(a) Calculate the fractional change in the concentration of vacancies at 300° C. How will this affect the diffusivity? Be quantitative in addition to qualitative.

(b) What would be the effect of a tensile strain of equal magnitude?