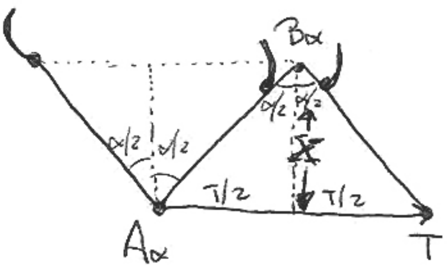
# P-Set 5 - STRUCTURE SOLUTIONS

1) a) $T_\perp \circ A_\alpha = B_\alpha$

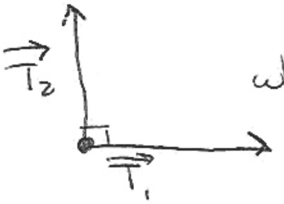


$\tan(\alpha/2) = \frac{T/2}{X}$ so $X = \frac{T}{2}\cot(\alpha/2)$

b) $\cos\varepsilon = \frac{(1-p)}{2}$ so if $p=1$ $\cos\varepsilon = 0$

$\varepsilon = 90°$ (or $\pi/2$ radians)

4-fold rotation symmetry means $\alpha = \pi/2$ $\{A_{\pi/2}, A_{\pi}, A_{3\pi/2}, 1\}$



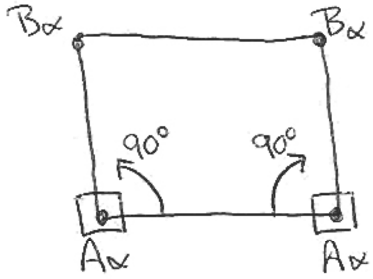
where $T_1 = T_2$

$T_1 \circ A_{\pi/2} = B_{\pi/2}$

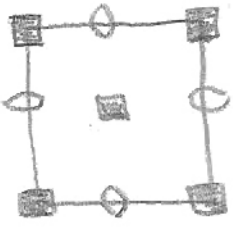
$T_1 \cdot A_{\pi} = B_{\pi}$

$T_1 \cdot A_{3\pi/2} = B_{3\pi/2}$

$T_1 \cdot A_1 = B_1$

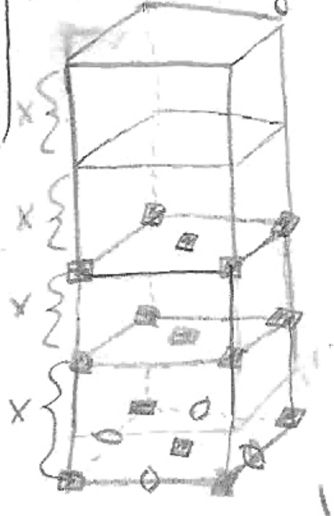


For P4



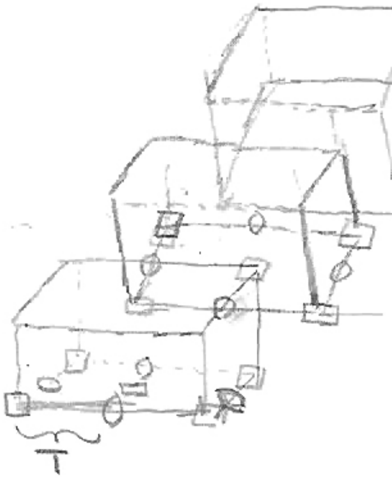
c) Two types of stacking based on symmetry requirements:

Normal Stacking



DISTANCE Between Planes is equal. Symmetry elements mapped normal to one another

Lateral Stacking



Lateral Stacking → Stack lattices but now there is a lateral translation of $\frac{1}{2}T$, but symmetry elements still

**3.012 PS 5**
Issued: 10.15.04
Due: 10.22.04

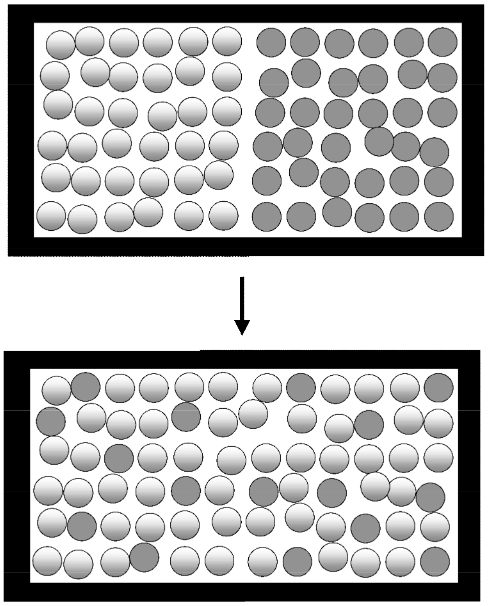
**3.012**
**Fall 2004**

---

2. **Formation of an ideal solution is always thermodynamically favorable.** Consider the mixing process described schematically below for an isolated two-component system.

   a. Using the ideal solution model of chemical potentials, show that at constant temperature and pressure, the Gibbs free energy change for taking an initially pure quantity of a component **A** and mixing it with a quantity of a second pure component **B** is always favorable (mixing will occur spontaneously) if the two components form an ideal solution.

   b. Show that the entropy change on mixing two components to form an ideal solution is always positive or zero. (Hint: How can I directly get the entropy change in the process from the Gibbs free energy change calculated in part (a)? Or in other words, how is S related to G?)



(a) The chemical potential of each component in an **A-B** ideal solution is:

$$\mu_A = \mu_{A,o} + RT \ln X_A$$
$$\mu_B = \mu_{B,o} + RT \ln X_B$$

To determine whether the mixing process will occur spontaneously, we need to calculate the Gibbs free energy change and determine if it is less than zero:

$$\Delta G_{mixing} = \Delta G_{system} = G_{final} - G_{initial} < 0?$$

The initial free energy of the system, for the unmixed components is simply:

$$G_{initial} = n_A \mu_{A,o} + n_B \mu_{B,o}$$

The free energy of the final state, where A and B have mixed to form an ideal solution is:

$$G_{final} = n_A\left(\mu_{A,o} + RT\ln X_A\right) + n_B\left(\mu_{B,o} + RT\ln X_B\right)$$

Combining these equations, the free energy change for the mixing process is:

$$\Delta G_{mixing} = G_{final} - G_{initial} = RT\left(n_A \ln X_A + n_B \ln X_B\right)$$

Because $X_A$ and $X_B$ are related, we can simplify this expression to:

$$\Delta G_{mixing} = RT\left(n_A \ln X_A + n_B \ln\left(1 - X_A\right)\right)$$

For a spontaneous process, ΔG must be less than zero:

$$n_A \ln X_A + n_B \ln\left(1 - X_A\right) < 0$$

Now, $n_A$ and $n_B$ are always positive numbers. The value of $X_A$ can range from 0-1. We see that for any value of $X_A$, the prescribed quantity will be negative in total, meaning that these liquids will mix in any ratio spontaneously- mixing is always favored.

(b) The entropy is always related to the Gibbs free energy by the partial derivative:

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,n}$$

…we know this from the complete differential expression for G:

$$dG = -SdT + VdP + \sum_i \mu_i dn_i = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{C} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i$$

Applying the partial derivative to our $\Delta G_{mixing}$, we obtain the entropy change on mixing:

$$\Delta S_{mixing} = -\left(\frac{\partial \Delta G_{mixing}}{\partial T}\right)_{P,n} = -\left[R\left(n_A \ln X_A + n_B \ln X_B\right)\right] = -R\left[n_A \ln X_A + n_B \ln\left(1 - X_A\right)\right]$$

The natural log terms in this expression are always less than or equal to zero- implying that the entropy on mixing for the ideal solution is always positive (or zero).