Answer Sheet 2

The terminology used here is as in the lecture notes.

1. Energy, defined relative to infinitely separated atoms, before mixing:

\[
\frac{1}{2} zN_a \left[ (1-x)(-2\epsilon_{AA}) + x(-2\epsilon_{BB}) \right]
\]

since the binding energy per pair of atoms is \(-2\epsilon\) and \(\frac{1}{2} zN_a\) is the number of bonds. After mixing, the corresponding energy is given by:

\[
\frac{1}{2} zN_a \left[ (1-x)^2(-2\epsilon_{AA}) + x^2(-2\epsilon_{BB}) + 2x(1-x)(-2\epsilon_{AB}) \right]
\]

where the factor of two in the last term is to count \(AB\) and \(BA\) bonds. Therefore, the change due to mixing is the latter minus the former, i.e.

\[
= -zN_a \left[ (1-x)^2(\epsilon_{AA}) + x^2(\epsilon_{BB}) + x(1-x)(2\epsilon_{AB}) \right]
\]

\[
- (1-x)(\epsilon_{AA}) - x(\epsilon_{BB})
\]

\[
= -zN_a \left[ -x(1-x)(\epsilon_{AA}) - x(1-x)(\epsilon_{BB}) + x(1-x)(2\epsilon_{AB}) \right]
\]

\[
= zN_a (x)(1-x)\omega
\]

given that \(\omega = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}\).

2. Examples of forces and their conjugate fluxes. \(z\) is distance, \(\phi\) is the electrical potential in Volts, and \(\mu\) is a chemical potential:

<table>
<thead>
<tr>
<th>Force</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electromotive force (e.m.f.)</td>
<td>(\frac{\partial \phi}{\partial z})</td>
</tr>
<tr>
<td>(-\frac{1}{T} \frac{\partial T}{\partial z})</td>
<td>Heat flux</td>
</tr>
<tr>
<td>(-\frac{\partial \mu}{\partial z})</td>
<td>Diffusion flux</td>
</tr>
</tbody>
</table>

We have seen that in an irreversible process, the product of the force \(Z\) and the flux \(J\) gives the rate of energy dissipation:

\[ T\sigma = JZ \]

where \(T\) is the temperature, \(\sigma\) is the rate of entropy production. \(T\sigma\) is therefore the rate of energy dissipation. In many cases, it is found experimentally that \(J \propto Z\).
When there is more than one dissipative process, the total energy dissipation rate can still be written

\[ T\sigma = \sum_i J_i X_i. \] (1)

In the case of grain boundary motion, the rate of energy dissipation is simply \( V\Delta G \) so that we immediately get

\[ V \propto \Delta G \]

An alternative is to consider the transfer of atoms across a grain boundary (a barrier of height \( Q \)). The probability of forward jumps (i.e. jumps which lead to a reduction in free energy) is given by

\[ \exp\{-Q/kT\} \]

whereas that of reverse jumps is given by

\[ \exp\{-(Q + \Delta G)/kT\} = \exp\{-Q/kT\} \exp\{-\Delta G/kT\} \]

The rate at which an interface moves is therefore given by

\[ V \propto \exp\{-Q/kT\}\left[1 - \exp\{-\Delta G/kT\}\right] \]

Note that this relation is hardly that predicted from irreversible thermodynamics. However, they become identical when \( \Delta G \) is small, i.e. there is not a great deviation from equilibrium. Note that for small \( x \), \( \exp\{x\} \simeq 1 + x \). Thus, at small driving forces,

\[ V_i \propto \exp\{-Q/kT\}\left[\Delta G/kT\right] \]

3. No, it is not independent, because although there is a steady state, there is flux of heat. Therefore, if you alter something in one of the planes it must affect all others. A steady state process is not at equilibrium.