

## 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.*

$$\begin{aligned} &= -zN_a \left[ (1-x)^2(\epsilon_{AA}) + x^2(\epsilon_{BB}) + x(1-x)(2\epsilon_{AB}) \right. \\ &\quad \left. - (1-x)(\epsilon_{AA}) - x(\epsilon_{BB}) \right] \\ &= -zN_a \left[ -x(1-x)(\epsilon_{AA}) + -x(1-x)(\epsilon_{BB}) + x(1-x)(2\epsilon_{AB}) \right] \\ &= zN_a(x)(1-x)\omega \end{aligned}$$

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:

Force	Flux
Electromotive force (e.m.f.) = $\frac{\partial\phi}{\partial z}$	Electrical Current
$-\frac{1}{T} \frac{\partial T}{\partial z}$	Heat flux
$-\frac{\partial\mu_i}{\partial z}$	Diffusion flux

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

$$T\sigma = \sum_i J_i X_i. \quad (1)$$

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

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

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,

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

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.