MSE-483 ADVANCED PHASE TRANSFORMATIONS

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NAME :

SCIPER :

Question	Points	Score
1	10	
2	15	
3	20	
4	20	
5	15	
6	20	
Total:	100	

Answer the questions in the space provided. Please ensure you show all your work and your answers are legible. If you need additional space, continue on the back of the page. You have 3 hours to complete the exam. **Good Luck!**

Difficult to remember formulas

1. Maxwell relations : $\left(\frac{\partial A}{\partial B}\right)_{\text{conjugate}(A)} = \pm\left(\frac{\partial(\text{conjugate}(B))}{\partial(\text{conjugate}(A))}\right)_B$
2. Fourier transform : $\mathcal{F}\{\frac{\partial^n c(t,x)}{\partial x^n}\} = (-ik)^n \tilde{c}(t,k)$

1. (a) (6 points) Derive the equilibrium criteria for two-phase coexistence (say between an α and β phase) in a binary A-B alloy at constant temperature, and pressure. The total number of A and B atoms, N_A and N_B are constant.

   (b) (4 points) Show that the chemical potential of A is equal to $\mu_A = G_m + (1 - x_A)\frac{\partial G_m}{\partial x_A}$, where $G_m = G/(N_A + N_B)$

a) Consider a system @ constant (T, p, N_A, N_B)

The characteristic potential is $G(T, p, N_A, N_B) = U - TS + pV$ ⇒ equilibrium is achieved when G is minimized

let there be 2-phases in the system: α & β

$G_{system} = G_\alpha + G_\beta \longrightarrow$ we have to minimize this to find equilibrium.

$dG_{system} = 0$ @ the minimum.

$$\Rightarrow \boxed{dG_\alpha + dG_\beta = 0} \text{ —— ①}$$

$G = U - TS + pV \Rightarrow dG = dU - TdS - SdT + pdV + Vdp$

The fundamental equation of thermodynamics $\Rightarrow dU = TdS - pdV + \sum_i \mu_i dN_i$

$$\boxed{dG = Vdp - SdT + \sum_i \mu_i dN_i}$$

$$dG^\alpha = V^\alpha dp - S^\alpha dT + \sum_i \mu_i^\alpha dN_i^\alpha \text{ ②} \quad ; \quad dG^\beta = V^\beta dp - S^\beta dT + \sum_i \mu_i^\beta dN_i^\beta \text{ ③}$$

We are at constant T & p ⟶ drop the temperature & pressure terms

Substituting equations ②, ③ in ①

$$\Rightarrow \sum_i \mu_i^\alpha dN_i^\alpha + \sum_i \mu_i^\beta dN_i^\beta = 0$$

Mass conservation $\Rightarrow N_i^\alpha + N_i^\beta = N_i$

$$\Rightarrow dN_i^\alpha = -dN_i^\beta$$

$$\Rightarrow dG = \sum_i (\mu_i^\alpha - \mu_i^\beta) dN_i^\alpha = 0$$

$$\boxed{\text{At equilibrium} \quad \mu_i^\alpha = \mu_i^\beta}$$

b) $dG = Vdp - SdT + \mu_A dN_A + \mu_B dN_B$

$$\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{p,T,N_B}$$

$$G^M = \frac{G}{N_A + N_B} \Rightarrow G = G^M (N_A + N_B)$$

$$\mu_A = \frac{\partial}{\partial N_A}\left(G^M (N_A + N_B)\right) = G_m + (N_A + N_B)\frac{\partial G_m}{\partial N_A} = G_m + (N_A + N_B)\left(\frac{\partial G_m}{\partial x_A}\right)_{T,p,N_B}\left(\frac{\partial x_A}{\partial N_A}\right)_{T,p,N_B}$$

$$\left(\frac{\partial x_A}{\partial N_A}\right)_{T,p,N_B} = \left[\frac{\partial}{\partial N_A}\left(N_A/_{N_A+N_B}\right)\right]_{T,p,N_B} = \frac{1}{N_A + N_B} - \frac{N_A}{(N_A + N_B)^2} = \frac{1 - x_A}{N_A + N_B}$$

$$\mu_A = G_m + \cancel{(N_A + N_B)} \times \frac{(1 - x_A)}{\cancel{N_A + N_B}}\left(\frac{\partial G_m}{\partial x_A}\right) = G_m + (1 - x_A)\left(\frac{\partial G_m}{\partial x_A}\right)_{T,p,N_B}$$

2. The phase diagram for a binary A-B alloy is shown in fig. 1

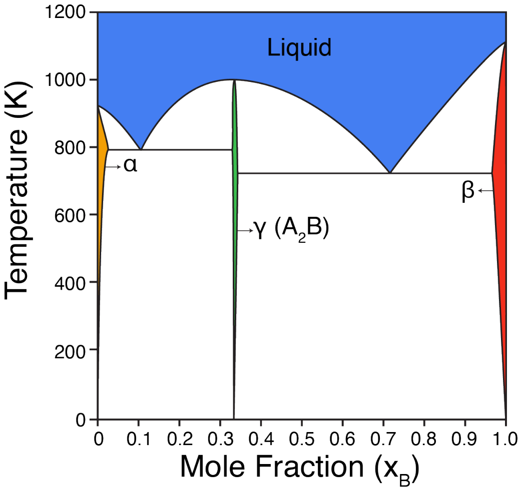
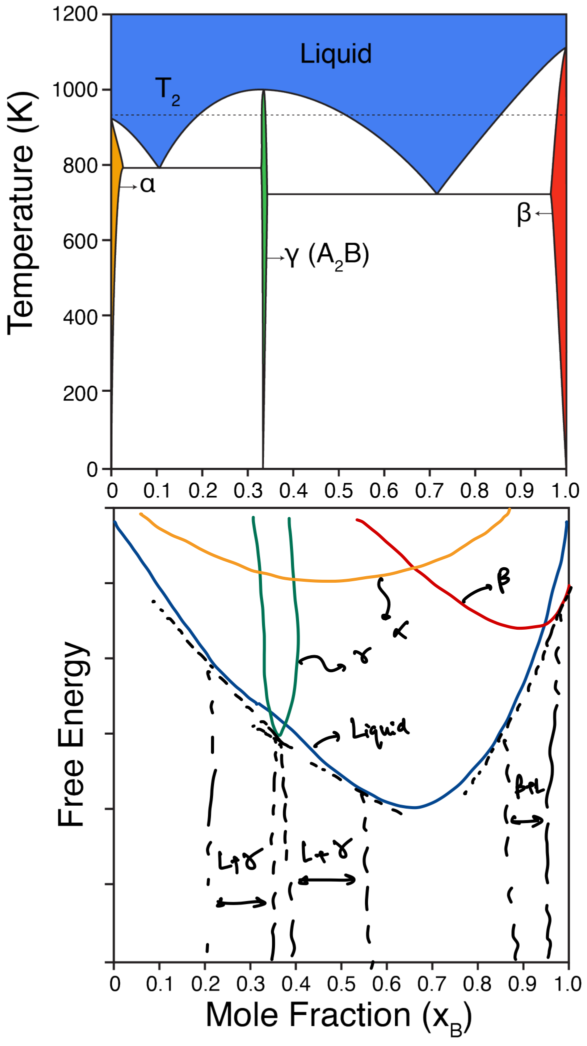
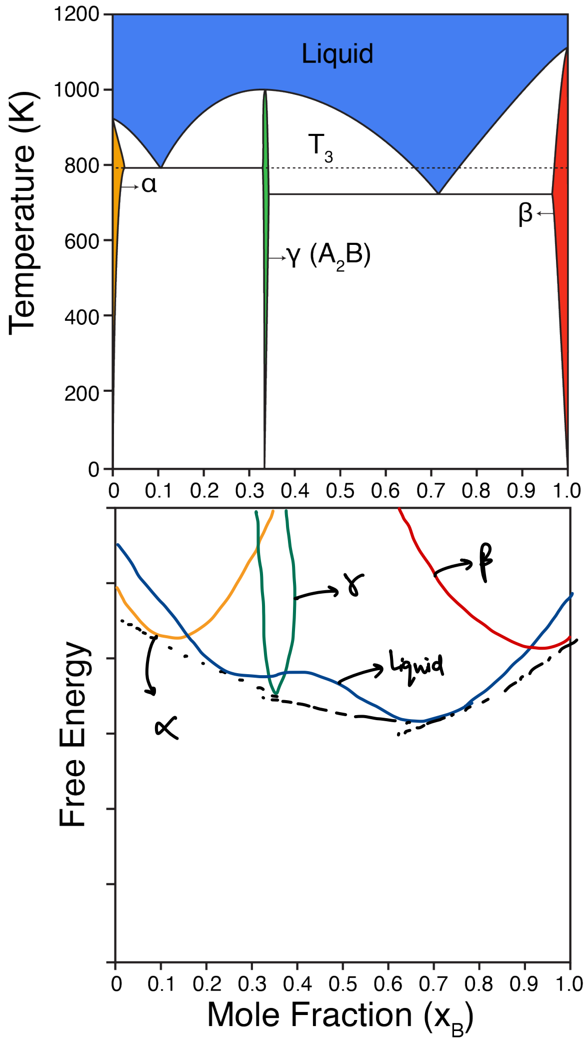


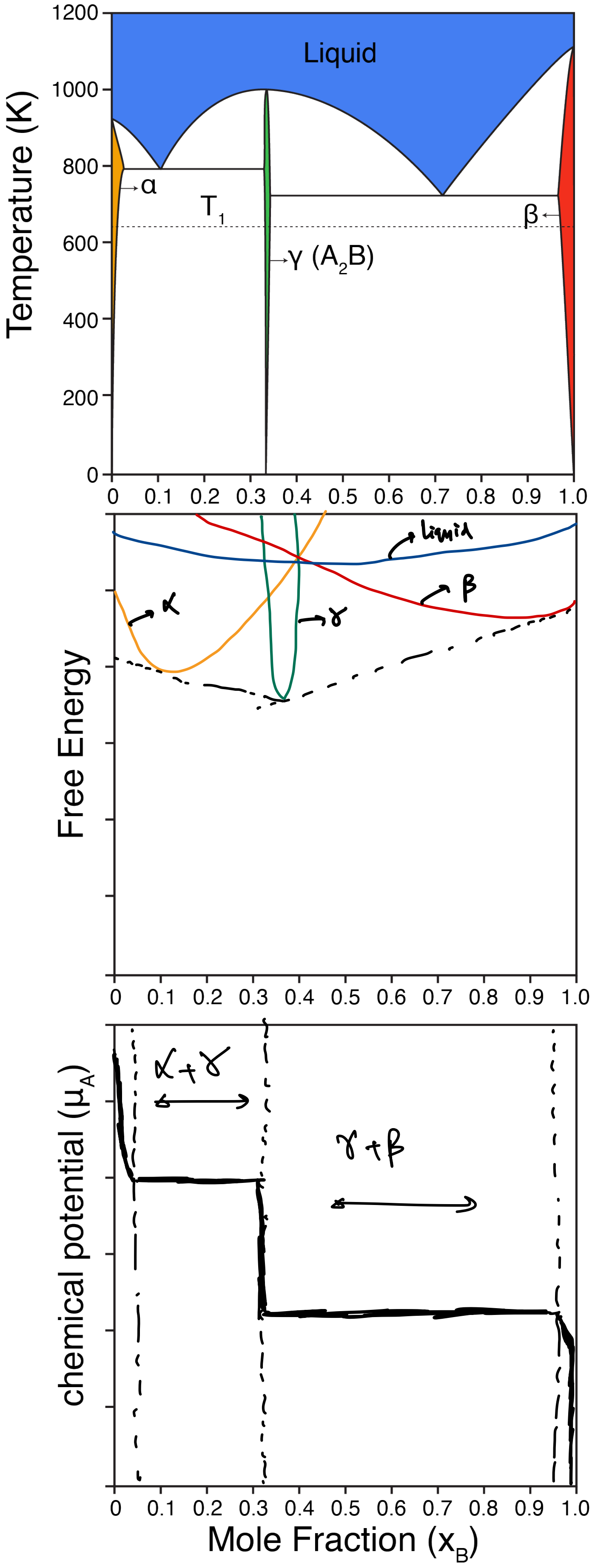
Figure 1

(a) (2 points) Consider an alloy with 50% A. If this alloy is held at 800K, which phases are present and what is their composition?

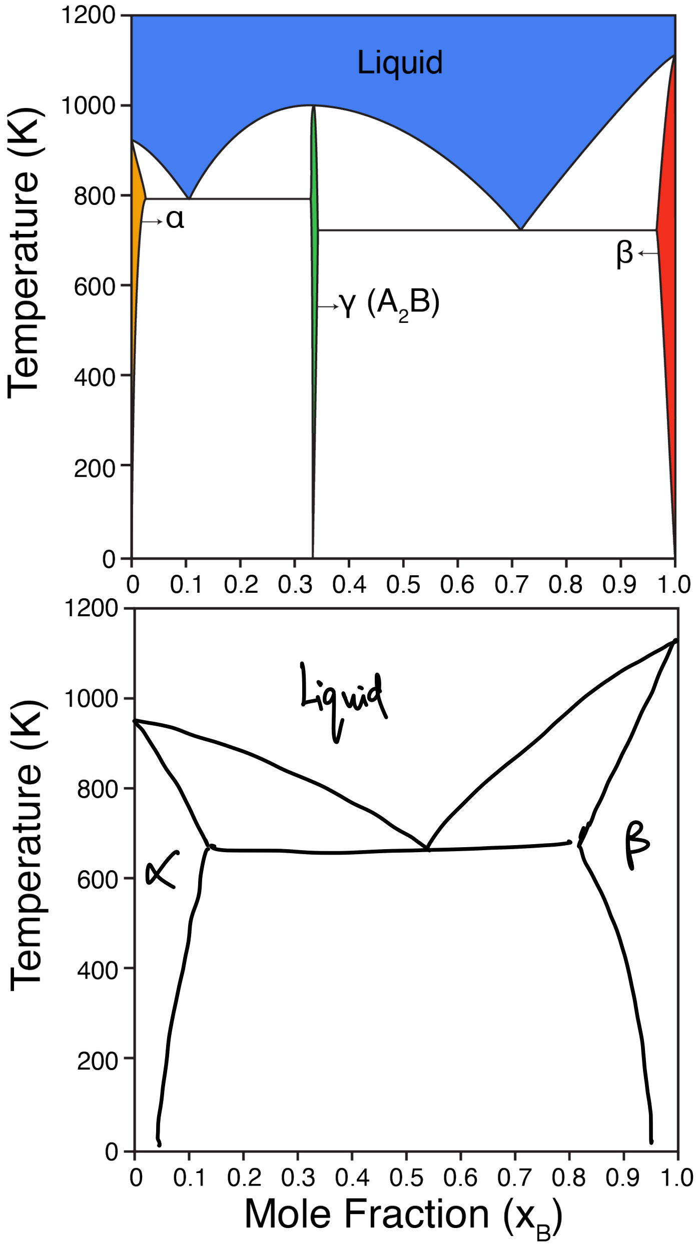
(b) (9 points) Sketch the free energies and chemical potentials of all the phases on the phase diagram at the indicated temperatures. Pay attention to the slopes, tangents, intercepts etc.






Temperature (K)
1200
1000
800
600
400
200
0
Liquid
α
T1
γ (A2B)
β
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Free Energy
liquid
α
γ
β
chemical potential (μA)
α + γ
γ + β
Mole Fraction (xB)

(c) (4 points) Schematically draw the phase diagram if the γ (A_2B) phase is prevented from forming.



3. A super-elastic single crystal can transform between two phases (α and β) which have different crystal structures. For the purposes of this problem, you can assume the phase transformation to be one-dimensional involving just a length change. At room temperature, a super-elastic strain of ϵ_0 can be achieved at an applied uniaxial stress of σ_0

   (a) (10 points) Define the relevant thermodynamic potential which is minized under conditions of constant applied force and temperature. Write down the equations of state of this potential and the matrix of second derivatives. You can neglect any work performed by/on the atmosphere.

   (b) (10 points) For a particular engineering application, the stress needed to achieve the super-elastic strain has to lie between $\sigma_1 < \sigma < \sigma_2$. Find an expression for the temperature range within which the material can operate.

   You are given the enthalpy of phase transition from $\alpha \rightarrow \beta$ is $\Delta H^{\alpha\rightarrow\beta} > 0$, molar volume $\overline{V}$ and the strain required to transform α to β is $\epsilon_0 < 0$. Please clearly state any assumptions you make in your derivation.

$$dU = TdS + fdL$$

$$\Rightarrow G(T,f) = U - TS - fL$$

$$\boxed{dG = -SdT - Ldf}$$

EOS: $\left(\frac{\partial G}{\partial T}\right)_f = -S \qquad \left(\frac{\partial G}{\partial f}\right)_T = -L$

Hessian:

$$\begin{bmatrix} \partial^2 G/\partial T^2 & \frac{\partial^2 G}{\partial T \partial f} \\ \frac{\partial^2 G}{\partial f \partial T} & \frac{\partial^2 G}{\partial f^2} \end{bmatrix} = \begin{bmatrix} -V\alpha & -V\gamma \\ -V\gamma & -V\beta \end{bmatrix}$$

$\longrightarrow$ 3 response functions.

(b) Along the coexistence line of α & β

$$-S^\alpha dT^* - L^\alpha df^* = -S^\beta dT^* - L^\beta df^*$$

$$\Rightarrow \frac{df^*}{dT^*} = -\frac{S^\beta - S^\alpha}{L^\beta - L^\alpha}$$

$$\frac{d\sigma}{dT} = -\frac{H^{\beta} - H^{\alpha}}{T^{*}(\varepsilon^{\beta} - \varepsilon^{\alpha})\bar{V}} = -\frac{\Delta H^{\alpha\to\beta}}{T^{*}\varepsilon_0 \bar{V}}. \longrightarrow ①$$

$H^{\beta} - H^{\alpha} = \Delta H^{\alpha\to\beta}$

$\varepsilon_0 = \varepsilon^{\beta} - \varepsilon^{\alpha}$

Assuming $\Delta H^{\alpha\to\beta}$, $\bar{V}$ and ε_0 are independent of T, we can integrate ①

$$\boxed{\Delta\sigma = \sigma(T_2) - \sigma(T_1) = -\frac{\Delta H^{\alpha\to\beta}}{\bar{V}\varepsilon_0} \log\left(T_2/T_1\right)}$$

use T_1 = room temperature to evaluate the limits in temperature for operation.

4. Oxides such as MgO typically contain equal numbers of positive and negatively charged vacancies when equilibrated at high temperatures. When the MgO crystal is placed in a uniform electric field, the vacancies will diffuse.
   (a) (12 points) Starting from the fundamental equation of thermodynamics, derive a flux relation for the charged species. Assume that the total numbers of both kinds of vacancies remains constant
   (b) (4 points) How many unique phenomenological coefficients are required to characterize transport in this system?
   (c) (4 points) What is an appropriate diffusion potential for the species in this problem? How could the diffusion potential be used to characterize steady state that would be achieved by annealing in an electric field for a very long time?

fundamental equation of thermo:

$$Tds = du - \phi dq^+ - \phi dq^- - \mu^+ dc^+ - \mu^- dc^-$$

$$dq^+ = (+2) dc^+$$

$$dq^- = (-2) dc^-$$

$$Tds = du - (2\phi + \mu^+) dc^+ - (\mu^- - 2\phi) dc^-$$

Time derivative + conservation of energy and mass

$$\boxed{T\dot{\sigma} = -\frac{\bar{J}_q}{T} \cdot \nabla T - \bar{J}_{c^+} \cdot \nabla(2\phi + \mu^+) - \bar{J}_{c^-} \cdot \nabla(\mu^- - 2\phi)}$$

$$\bar{J}_q = -L_{qq}\frac{\nabla T}{T} - -L_{c^+q}\nabla(\mu^+ + 2\phi) - L_{c^-q}\nabla(\mu^- - 2\phi)$$

$$\bar{J}_{c^+} = -L_{c^+q}\frac{\nabla T}{T} - L_{c^+c^+}\nabla(\mu^+ + 2\phi) - L_{c^+c^-}\nabla(\mu^- - 2\phi)$$

$$\bar{J}_{c^-} = -L_{c^-q}\frac{\nabla T}{T} - L_{c^+c^-}\nabla(\mu^+ + 2\phi) - L_{c^-c^-}\nabla(\mu^- - 2\phi)$$

6 phenomenological constants.

c) Diffusion potentials will have the form as shown above:
At eq^m the diffusion potentials (ie) $(\mu^+ + 2\phi)$, $(\mu^- - 2\phi)$, T
will be uniform in space.

5. Consider the formation of a solid nucleus of phase α within a liquid phase at a temperature T. At this temperature, the liquid phase is metastable and the solid phase is stable. The free energy change per unit volume for the formation of α from the liquid is $\Delta g^{l\rightarrow\alpha}$. The interfacial energy for a cuboidal and spherical nucleus are given by γ_c and γ_s respectively.
   (a) (5 points) Write down the free energy change for an entirely liquid system to form a cuboidal nucleus of the α phase with dimensions of $a \times a \times b$
   (b) (5 points) What is the critical nucleation size for a cuboidal nucleus? Express your answers in terms of $\gamma_c, \Delta g^{l\rightarrow\alpha}, \gamma_s$
   (c) (5 points) How does the free energy barrier to form a cuboidal nucleus compare to the free energy of a spherical nucleus containing the same quantity of matter?

(a) $$\Delta G = \underbrace{(\Delta g^{l\rightarrow\alpha})\, a^2 b}_{\uparrow \text{ free energy gain}} + \underbrace{\gamma_c\,(2a^2 + 4ab)}_{\uparrow \text{ interfacial energy penalty.}}$$

(b) $\Delta G(a,b) \longrightarrow$ to find the maximum. both $\frac{\partial \Delta G}{\partial a}$ and $\frac{\partial \Delta G}{\partial b}$ must equal zero.

$$\Rightarrow \frac{\partial \Delta G}{\partial a} = 2ab\, \Delta g^{l\rightarrow\alpha} + 4a\gamma_c + 4b\gamma_c = 0$$

$$\frac{\partial \Delta G}{\partial b} = \Delta g^{l\rightarrow\alpha} a^2 + \gamma_c \times 4a = 0$$

$$\Rightarrow \boxed{a = \begin{cases} 0 \\ \dfrac{-\gamma_c \times 4}{\Delta g^{l\rightarrow\alpha}} \end{cases}}$$

$$\Rightarrow -\frac{8\gamma_c}{\Delta g^{l\rightarrow\alpha}}\, b\, \Delta g^{l\rightarrow\alpha} - \frac{16\gamma_c^2}{\Delta g^{l\rightarrow\alpha}} + 4b\gamma_c = 0$$

$$\Rightarrow \boxed{b = -\frac{4\gamma_c}{\Delta g^{l\rightarrow\alpha}}}$$

(c) Amount of matter in critical nucleus:

$$a^2 b = \frac{-16\gamma_c^2 \times 4\gamma_c}{(\Delta g^{l\rightarrow\alpha})^3} = -64\left(\frac{\gamma_c}{\Delta g^{l\rightarrow\alpha}}\right)^3 = \frac{4}{3}\pi r^3 \longrightarrow \text{for a sphere of the same size.}$$

$$\boxed{r^3 = -\frac{48}{\pi}\left(\frac{\gamma_c}{\Delta g^{l\rightarrow\alpha}}\right)^3}$$

$$\Delta G_{\text{spherical}} = \frac{4}{3}\pi r^3 \Delta g^{l\to\alpha} + 4\pi r^2 \gamma_s$$

$$= 4\pi r^2 \left[\frac{r}{3} \Delta g^{l\to\alpha} + \gamma_s \right]$$

$$= 4\pi \left(\frac{48}{\pi}\right)^{2/3} \left(\frac{\gamma_c}{\Delta g^{l\to\alpha}}\right)^2 \left[-\left(\frac{48}{\pi}\right)^{1/3} \gamma_c + \gamma_s \right] = 4\pi \left(\frac{48}{\pi}\right)^{2/3} \left[\frac{\gamma_c^3}{(\Delta g^{l\to\alpha})^2}\right] \left[\frac{\gamma_s}{\gamma_c} - \left(\frac{48}{\pi}\right)^{1/3}\right]$$

$$\Delta G_{\text{cuboid}} = a^2 b \,\Delta g^{l\to\alpha} + \gamma_c (4ab + 2a^2)$$

$$\boxed{\Delta G_c = \frac{32\gamma_c^3}{\Delta g^2}}$$

$$\boxed{\frac{\Delta G_s}{\Delta G_c} = \frac{4\pi}{32}\left(\frac{48}{\pi}\right)^{2/3} \left[\frac{\gamma_s}{\gamma_c} - \left(\frac{48}{\pi}\right)^{1/3}\right]}$$

6. Figure 3 is a transmission electron micrograph of the microstructure after an ordered FeAl crystal with the CsCl structure is cooled into a miscibility gap and held there for an extended time. Bright regions are ordered and higher in Al content while dark regions are disordered and lower in Al. The long curved dark line is an antiphase boundary.

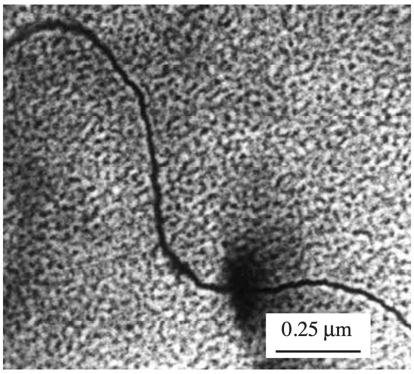


Figure 3: Microstructure of a phase separated Fe-24 at.% alloy (from Allen & Russell)

(a) (5 points) Schematically sketch the crystal structure showing the atomic arrangements across the anti-phase boundary. How many variants of the ordered structure exist?

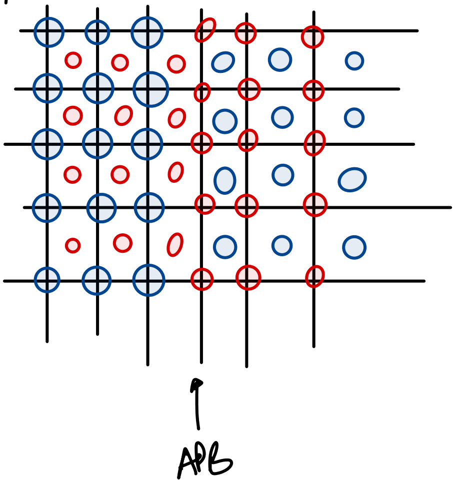
(b) (3 points) Qualitatively describe the phase transformations that the system has undergone to attain the microstructure shown in fig. 3.

(c) (4 points) Write down an expression for the total free energy of the system as a function of a homogeneous free energy density and any other phenomenological material constants you might require.

(d) (4 points) Measurements of the elastic constants in Fe-Al indicate that the alloy is highly elastically anisotropic. Considering the microstructure in fig. 3, why is this surprising?

(e) (4 points) Measurements of the lattice constant in the alloy over a range of compositions and temperatures show that the lattice constant increases with Al content in disordered alloys and that increasing long-range order decreases the lattice constant. Explain how this could be used to rationalize the microstructure in fig. 3.

a)



2 variants of the B2 phase.

b) Ordering phase transition to form the APB followed by spinodal decomposition to form the mottled region.

(c)

$$G = \iint_V \left[g\left(x(\vec{r}), \eta(\vec{r}), T\right) + \sum_{\alpha\beta} K_{\alpha\beta}\left(x(\vec{r})\right) \frac{\partial x}{\partial r^\alpha} \frac{\partial x}{\partial r^\beta} + \sum_{\alpha\beta} N_{\alpha\beta}\left(\eta(\vec{r})\right) \frac{\partial \eta}{\partial r^\alpha} \frac{\partial \eta}{\partial r^\beta} \right] \frac{d\vec{r}}{\Omega}$$

homogeneous free energy

gradient energy coefficient penalizes concentration profiles with large gradients

Order parameter gradient energy term

(d) The microstructure looks rather isotropic. Assuming all interfaces are coherent, certain directions in the crystal structure would be elastically softer due to anisotropy. This should lead to microstructures that are anisotropic - contrary to what is observed.

(e) The $\eta(\vec{r})$ & $x(\vec{r})$ fields likely evolve to reduce the misfit strain between the ordered and disordered phases.