Midterm Solutions
Problem 1. (1p)

Considering basic definitions of enthalpy (H) and Gibbs free energy (G; where p-pressure, U-internal energy, V-total volume, T- absolute temperature, S-total entropy):

\[ H = U + pV \text{ and } G = U - TS + pV. \]

Using 1\textsuperscript{st} and 2\textsuperscript{nd} Law of Thermodynamics show (derive) that:

\[ dH + dG = TdS - SdT \]

\[ dQ = dU + pdV \rightarrow 1\textsuperscript{st}. \quad dQ = TdS \rightarrow 2\textsuperscript{nd} \]

\[ H = U + pV : \quad dH = \frac{\partial U}{\partial T}dT + \frac{\partial U}{\partial V}dV + \frac{\partial U}{\partial p}dp \]

\[ \Rightarrow dH = TdS + pdp \]

\[ G = U - TS + pV : \quad dG = \frac{\partial U}{\partial T}dT - \frac{\partial S}{\partial T}dS - \frac{\partial S}{\partial S}dS + \frac{\partial V}{\partial T}dT + \frac{\partial V}{\partial p}dp \]

\[ \Rightarrow dG = TdS + pdS - SdT + pdp \]

\[ \Rightarrow dH + dG = TdS - SdT + 2pdp \]
Problem 2 (2p)

Consider spherical shape of Pt nanoparticle. For Pt, $\gamma = 2 \text{ J/m}^2$, $K_T = 800 \text{ MPa}$. Find out at what diameter the Pt nanoparticle energy related to its surface is equal to the nanoparticle strain energy related to the phenomenon of Laplace pressure. Calculate the strain value (%) for this nanoparticle? Make the comment if such nanoparticle can/can’t exist in reality and why?

\[ \text{Laplace: } \Delta p = \frac{2\gamma}{R} \]
\[ E_{\text{strain}} = \frac{1}{2} \Delta p \cdot \varepsilon \quad \text{Hooke's law } \varepsilon = \frac{\Delta p}{K_T} \]
\[ E_{\text{strain}} = \frac{1}{2} \cdot \frac{\Delta p^2}{K_T} \left[ \frac{1}{3} \right] \]
\[ E_{\text{strain}} [J] = \frac{1}{2} \cdot \frac{\Delta p^2}{K_T} \cdot V_{\text{ nanoparticle}} = E_{\text{strain}} = A_{\text{ nanoparticle}} \cdot \varepsilon \quad [J] \]

\[ \frac{\Delta p^2}{K_T} = 2 \gamma \cdot \frac{A_{\text{ nanoparticle}}}{V_{\text{ nanoparticle}}} \]
\[ \frac{A_{\text{ nanoparticle}}}{V_{\text{ nanoparticle}}} = \frac{3}{R} \quad \Delta p^2 = \frac{4\gamma^2}{K_T^2} \]

\[ \frac{2\gamma^2}{K_T^2} = 2\gamma \cdot \frac{3}{R} \quad \Rightarrow R = \frac{2\gamma}{\frac{3}{K_T}} = \frac{2 \times 2 \times 10^{-8} \frac{\text{J}}{\text{m}^2}}{3 \times 2 \times 10^{-10} \frac{\text{m}^3}{\text{m}^3}} = \frac{1}{3} \times 10^6 \text{m} \]

\[ R = \frac{2 \gamma}{3 K_T} = \frac{2 \times 2 \times 10^{-8} \frac{\text{J}}{\text{m}^2}}{3 \times 2 \times 10^{-10} \frac{\text{m}^3}{\text{m}^3}} = \frac{1}{3} \times 10^6 \text{m} \]
Problem 2 (2p)

Consider spherical shape of Pt nanoparticle. For Pt, $\gamma = 2 \text{ J/m}^2$, $K_v = 800 \text{ MPa}$. Find out at what diameter the Pt nanoparticle energy related to its surface is equal to the nanoparticle strain energy related to the phenomenon of Laplace pressure. Calculate the strain value (%) for this nanoparticle? Make the comment if such nanoparticle can/can’t exist in reality and why?

$$E = \frac{6P}{K_v} = \frac{2\pi}{RK_v} = \frac{2\times2 \cdot 10^{-9}}{1.6\times10^{-10} \times 8\times10^8 \cdot \frac{2}{m^3}}$$

$$E = 3 \times 300\% = 900\% \quad \text{TOO LARGE FOR A REAL MATERIAL, CANNOT EXIST.}$$
Problem 3 (2p)

Consider two cubic nanoparticles with same lateral dimension 'a=20 nm'. They are made of the same material (Au). Assume they are fused into a new nanoparticle with symmetrical shape which has the characteristic dimension 'b', and surface to volume ratio \( \sim 4/b \). If the spike in temperature of the new nanoparticle immediately after the fusion process is 120 K find out what is the value of b \( (\gamma = 2 \text{ J/m}^2, \ C_p = 4200 \text{ J/(gK)}^2, \ \rho = 20 \text{ g/cm}^3) \).

\[
\begin{align*}
\Delta \text{E}_{\text{np}} &= \frac{4}{b} \\
V_{\text{np}} &= 2a^3 \\
A_{\text{np}} &= 6a^2 \\
V_{\text{fnp}} &= a^3 \\
C_p \cdot S \cdot V_{\text{fnp}} \cdot \Delta T &= (2A_{\text{np}} - A_{\text{fnp}}) \cdot \Delta T \\
C_p \cdot S \cdot \Delta T &= \left(2 \frac{A_{\text{np}}}{V_{\text{fnp}}} - \frac{A_{\text{fnp}}}{V_{\text{fnp}}} \right) \cdot \Delta T \\
C_p \cdot S \cdot \Delta T &= \left(\frac{6}{a} - \frac{4}{b}\right) \cdot \Delta T = \frac{6}{a} - \frac{4}{b} = \frac{C_p \cdot S \cdot \Delta T}{a - b}
\end{align*}
\]
Problem 3 (2p)

Consider two cubic nanoparticles with same lateral dimension ‘a=20 nm’. They are made of the same material (Au). Assume they are fused into a new nanoparticle with symmetrical shape which has the characteristic dimension ‘b’, and surface to volume ratio \(\sim \frac{4}{b}\). If the spike in temperature of the new nanoparticle immediately after the fusion process is 120 K find out what is the value of b (\(\gamma = 2 \text{ J/m}^2\), \(C_p = 4200 \text{ J/(gK)}\), \(\rho = 20 \text{ g/cm}^3\)).

\[
\frac{6}{a} - \frac{4}{b} = \frac{C_p \delta T}{\rho} \quad \Rightarrow \quad \frac{6}{a} - \frac{C_p \delta T}{\rho} = \frac{4}{b}
\]

\[\therefore \quad b = \frac{6}{\frac{6}{a} - \frac{C_p \delta T}{\rho}}
\]
Problem 4 (2p)

a) In a maximum three sentences describe: i) what is the Landau’s ordering parameter M, ii) how
different you expect to have M for 3 nm nanoparticle vs. 3 cm of solid made of the same
material. iii) What is the max and min value of M.

- M DESCRIBES ORDER IN CRYSTALINE MAT.
- \( M(3\text{nm}) < M(\text{bulk}) \) — \( M_{\text{max}} = 1 \); \( M_{\text{min}} = 0 \)

b) On the graph below, the dependence of the M is graphed as a function of nanoparticle size for
surface and center (core) of nanoparticle. Indicate what curve belongs to surface and what for
core of the nanoparticle.

← This figure is in the book
Fig 3.20
Read text associated with this figure
Problem 5 (2p)

a) The difference in free energy of two phases (BCC and FCC) of Fe is 0.4 kJ/mol where BCC is more stable phase. For a Fe nanoparticle that contains 1000 atoms, find out at what temperature the thermal fluctuations will lead to existence of both phases in nanoparticle.

\[ \Delta g_{\text{FCC} - \text{BCC}} = \frac{0.4 \times 10^3}{6.023 \times 10^{23}} \text{ J/atom} \]

\[ \Delta g_{\text{FCC} - \text{BCC}} = \frac{0.4 \times 10^3}{6.023 \times 10^{23}} \]

\[ kT_B = 500 \times \frac{\Delta g}{N_A} \]

\[ T = \frac{500 \times 400}{N_A \cdot k_B} = \frac{500 \times 400}{N_A \cdot k_B} \]

\[ T \approx 20000 \text{ K} \]

Assume that fluctuations transfer so.

Of particle from BCC + FCC!
b) What is the origin of superparamagnetism in ferromagnetic nanoparticles? When and why does this happen, explain.

READ BOOK; in short:

\[ K_u \gg V \text{ for } V \text{ very small} \]

\[ K_u \ll k_B T \quad \text{thermal fluctuation become larger than magnetic anisotropy energy} \]

\[ V \ll K_u \]

\[ \tau = T_0 \exp \left( \frac{K_u}{kT} \right) \quad \text{stability of magnetization} \]

\[ \tau \propto \text{no. relaxation time, magnetization} \]
Problem 6. (2p)
a) In the graph below, a schematic of the process for nanoparticle synthesis is shown with the most important parts. i) What is the purpose of the arc in the schematics, ii) what is the typical type of nanoparticle produced using this process?

b) In the graph below there are two different collision parameter dependences for different nanoparticles. Explain why collision parameters vs. nanoparticle size trends differ in these two graphs, what is the reason?

Fig 4.4 from the book
- Read text related to the process.
- Arc, intense and evaporates metal precursor rod.
- Metal oxide NP

Fig 4.6
- Read text in the book
Left (charged NP)
Right (low-charge NP)
Problem 7. (1p)

In the figure below, there are schematics of four different nanoparticle synthesis apparatuses/processes. Indicate (check mark) which one is the “nanoparticle synthesis using inert gas condensation process”? What is the typical range of microwave frequency in “microwave plasma system for nanoparticle synthesis”?

\[ \sim 6 \text{ GHz} \]

At the same page with Fig. 8.19, you have info about f of MPS

Fig. 4.8 in Book
Problem 8 (2p)

a) Consider FePt and CoPt L10 particles which have the same size, R = 25 nm. Which ones should be more stable if used for magnetic recording bit pattern media application at T ranging between 200 and 500 K and how many times. (K_{u,CoPt} = 5 kJ/m^3 K_{u,FePt} = 7.5 kJ/m^3).

\[ K_{u,FePt} > K_{u,CoPt}, \text{ so FePt L10 is more stable} \]

How many times:

\[ \frac{P_{FePt}}{P_{CoPt}} = \frac{P_0 \exp \left( \frac{K_{u,FePt} V}{kT} \right)}{P_0 \exp \left( \frac{K_{u,CoPt} V}{kT} \right)} = \exp \left( \frac{K_{u,FePt} - K_{u,CoPt}}{kT} \right) = \exp \left( \frac{(2.5 \text{ kJ/m}^3) \cdot V}{kT} \right) \]

\[ \frac{P_{FePt}}{P_{CoPt}} \]

For T = 200 °C, \[ \frac{P_{FePt}}{P_{CoPt}} \]

\[ \frac{P_{FePt}}{P_{CoPt}} \]
b) What happens with coercivity of nanoparticles as their size decreases?

I would accept any reasonable answer with logic.

- If you look the slides from W521
  the full study is presented in this graph

\[ H_c = \frac{2K}{\mu_0 M_s} \]

- However, would accept even partial description.
Problem 9 (1p)

Assume that the near surface region of CoFe nanoparticle has saturation magnetization which is 1/2 of the one for the bulk material (Ms=2.4 T). The thickness of near surface region is 0.5 nm. Assuming the cubic CoFe nanoparticle, and that the Ms of NP is volume average of Ms for bulk and near surface region find out what is the saturation magnetization for nanoparticle with a=4 nm, and a=10 nm. Which particle has larger coercivity?

\[
M_{NP} = \frac{V_s}{V_{tot}} M_{ss} + \frac{V_B}{V_{tot}} M_{ss,B}
\]

\[
V_{tot} = V_s + V_B
\]

\[
M_{NP} = \frac{V_s}{V_{tot}} M_{ss} + \frac{V_B}{V_{tot}} M_{ss,B}
\]

\[
V_s = a^3 - (a-2\delta)^3 \quad V_B = (a-2\delta)^3
\]

\[
M_{NP} = \frac{a^3 - a^3 + 2a^2\delta - 4a\delta^2 + \delta^3}{a^3} M_{ss} + \frac{a^3 - 2a^2\delta + 4a\delta^2 - 3\delta^3}{a^3} \times M_{ss,B}
\]

\[
M_{NP} = \left( \frac{2\delta}{a} - \frac{4\delta^2}{a^2} + \frac{\delta^3}{a^3} \right) M_{ss} + \left( 1 - \frac{2\delta}{a} + \frac{4\delta^2}{a^2} - \frac{\delta^3}{a^3} \right) \times M_{ss,B}
\]
\[ a_1 = 4 \times 10^{-9} \text{m} ; \quad a_2 = 2 \times 10^{-9} \text{m} ; \quad \delta = 0.5 \times 10^{-9} \text{m} \]

\[ N_{s,1} = 1.27 \quad ; \quad N_{s,1} = 2.47 \]

\[ M_{\text{np}} \left( \frac{2\delta}{a} - \frac{4\delta^2}{a^2} + \frac{\delta^3}{a^3} \right) N_{s,1} + \left( 1 - \frac{2\delta}{a} + \frac{4\delta^2}{a^2} - \frac{\delta^3}{a^3} \right) N_{s,1} \]

\[ M_{\text{np}, a=20} = \ldots \ldots \]

\[ M_{\text{np}, a=4} = \ldots \ldots \]

\[ \Rightarrow M_{\text{np}, a=20} > M_{\text{np}} = 4 \text{m} \]
Problem 10. (1p)

The shape of the stable nucleus is cube. In a step by step process as done in the class, derive the critical dimension (side of the cube) of the smallest stable nucleus for this case. Derive what is the free energy of the smallest stable nucleus. What do you think will happen if the strain energy is taken into account, will the size of the smallest stable nucleus increase or decrease?

\[
\begin{align*}
\Delta G &= \frac{a^3}{8}\mu - 6a^2x \delta \\
\Delta G_x &= -\frac{\mu}{V^m} (\delta \mu) + 4a \delta \\
\Delta G_m &= -\frac{a^3}{V^m} (\delta \mu) + 6a^2x \\
\frac{\partial \Delta G}{\partial a} &= 0 \\
12a \delta &= \frac{3a^2}{V^m} \delta \mu \\
\Rightarrow \Delta a &= \frac{4\delta \mu}{3a} = \frac{4\delta \mu V^m}{3a^2}
\end{align*}
\]
Problem 10. (1p)

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\[ V = a^3 \]
\[ A = 6a^2 \]
\[ V_s \left[ \frac{1}{3} \right], \quad V_s \times V [J] \]
\[ U_s \left[ \frac{1}{4} \right] \]

**STRAIN ENERGY**

\[ U_s = \frac{1}{2} k_v e^2 \]

\[ \Delta G_m = - \frac{a^3(\Delta \mu)}{\sigma_a} + 6e^2 x + \frac{1}{2} k_v e^2 a^3 \]

\[ \sigma_m \]

\[ \frac{\partial \Delta G_m}{\partial a} = 0 \]

\[ \frac{3a^2}{2} \sigma_m = 12a x + \frac{3}{2} k_v e^2 a^2 \]

\[ a^2 \left( \frac{3\sigma_m}{2\sigma_m} - \frac{3}{2} k_v e^2 \right) = 12 a x \]

\[ \left( \frac{3\sigma_m}{2\sigma_m} \right) = \frac{12 a x}{48 - \frac{1}{2} k_v e^2} = \frac{48 - \frac{1}{2} k_v e^2}{\sigma_m - \frac{1}{2} k_v e^2} \]

\[ \sigma_m \]

\[ \Delta a \]

\[ \Delta \mu \]
\[ a^* \leq a_1^* \quad a_s^* = \frac{48 \nu_{ms}}{9 \mu - \frac{1}{2} k_s \varepsilon_0} \]

\[ \Delta \mu > \frac{1}{2} k_s \varepsilon_0 - \frac{\Delta \mu}{\sigma_m} \Rightarrow a^* < a_2^* \]

\[ \Delta \xi_{1S} = -\frac{a_s^{*3}}{\sigma_m} \Delta \mu + 6a_s^{*2} \sigma + \frac{1}{2} k_s \varepsilon_0 a_s^{*3} \]

\[ \Delta \xi_{2S} = a_s^{*3} \left( \frac{1}{2} k_s \varepsilon_0 - \frac{\Delta \mu}{\sigma_m} \right) + 6a_s^{*2} \sigma \]

\[ \Delta \xi_{1S} > \Delta \xi_{2S} \]

\[ 6a_s^{*2} \sigma > 6a^0 \sigma \]