Midterm for Thermal Physics (II)
Date: May 7, 2012

(1) Please do not flip the sheet until instructed.
(2) Please try to be as neat as possible so that I can understand your answers without ambiguity.
(3) While it is certainly your rights to make wild guesses or memorize irrelevant details, I would truly appreciate if you try to make your answers logical.
(4) Good luck for all hard-working students!

Lecturer: Hsiu-Hau Lin

Midterm for Thermal Physics (II)
Date: May 7, 2012

1. Binary mixture (20%) Consider a simple model for a binary mixture $A_{1-x}B_x$ in two dimensions. The average number of surrounding neighbors is 6 and the potential energies for A−A, B−B and A−B bonds are $u_{AA} = 3\Delta$, $u_{BB} = -2\Delta$ and $u_{AB} = \Delta$ accordingly, where Δ is some positive constant. **(a)** Find the free energy $f(x)$ of the binary mixture. **(b)** Sketch the phase diagram and highlight the solubility gap.

2. Solidification of a binary alloy (20%) Consider a binary alloy $A_{1-x}B_x$ with the solidification temperatures $\tau_A > \tau_B$. For simplicity, assume neither the solid nor the liquid has a solubility gap. **(a)** Sketch the free energies $f_S(x)$ and $f_L(x)$ for the solid and the liquid at three different temperature regimes: (1) $\tau > \tau_A$ (2) $\tau_B < \tau < \tau_A$ (3) $\tau < \tau_B$. **(b)** Construct the phase diagram and explain how the solidification of a binary alloy proceeds upon cooling.

3. Minimum conductivity in semiconductor (20%) The electrical conductivity in a semiconductor is

$$\sigma = en_e\tilde{\mu}_e + en_h\tilde{\mu}_h$$

where $\tilde{\mu}_e$ and $\tilde{\mu}_h$ are the electron and hole mobilities. The quantum concentrations for conduction and valence bands are n_c and n_v with a band gap ϵ_g and the electron gas is non-degenerate. **(a)** Find the conductivity σ_{int} for an intrinsic semiconductor. **(b)** For most semiconductors, $\tilde{\mu}_e > \tilde{\mu}_h$. The minimum conductivity can be reached in a p-type semiconductor. Find the minimum conductivity σ_{min} and compare with the intrinsic conductivity σ_{int}.

4. Potential profile in $p-n$ junction (20%) Near the interface of a $p-n$ junction, electrons and holes annihilate each other, creating a depletion zone. The width of the depletion zone of the $p-$type side is w_p and that on the $n-$type side is w_n. The charge distribution in a $p-n$ junction can be approximated as,

$$\rho(x) = \begin{cases} -en_a, & 0 < x < w_p; \\ en_d, & -w_n < x < 0; \\ 0, & \text{otherwise.} \end{cases}$$

The widths w_p, w_n need to be solved from the Poisson equation for the electrostatic potential $\varphi(x)$. The boundary conditions are $\varphi(-\infty) = 0$ and $\varphi(+\infty) = -V_{bi}$. Find the electric field $E(0)$ at the interface of the junction.

5. Joule-Thomson effect (20%) Investigate the Joule-Thomson effect in a van der Waals gas described by

$$P = \frac{N\tau}{V - Nb} - \frac{N^2 a}{V^2} \approx \frac{N\tau}{V} + \left(\frac{N^2 b\tau}{V^2} - \frac{N^2 a}{V^2}\right),$$

where the corrections arisen from the finite volume of molecules and the inter-molecular attraction. Explain the constancy of enthalpy, ideal gas expansion and the Joule-Thomson effect for a van der Waals gas in detail.

6. Recombination of electrons and holes (Bonus 20%) Consider a semiconducting device at nanoscale. There are N_c conduction orbitals at energy ϵ_c and N_v valence orbitals at energy ϵ_v. The average electron number in the conduction orbitals is N_e and the average hole number in the valence orbitals is N_h. The decay rate for an electron tunneling from an occupied conduction orbital to an empty valence orbital is γ and the rate for the reverse process is γ'. **(a)** Compute the recombination rate $R_{c\to v}$ from the conduction orbitals to the valence orbitals and the rate $R_{v\to c}$ for the reverse processes. **(b)** Make use of detail balance in thermal equilibrium to express γ' in terms of γ. Note that Fermi-Dirac distribution should be used here to account for quantum statistics. Find the total recombination rate R for electrons and holes.

HH0044 Midterm Solution

1. Binary mixture. The average interaction of an atom A is

$u_A = (1-x)\,u_{AA} + x\,u_{AB}$. Similarly, $u_B = (1-x)\,u_{AB} + x\,u_{BB}$.

The internal energy for one atom then is

$$u = \frac{1}{2}\cdot 6 \cdot \left[(1-x)\,u_A + x\,u_B \right] = 3\left[(1-x)^2 u_{AA} + x^2 u_{BB} + 2x(1-x)\,u_{AB} \right]$$

$$= \Delta\left(-3x^2 - 12x + 9\right)$$

The mixing entropy for each atom is

$$\sigma = -x\log x - (1-x)\log(1-x).$$

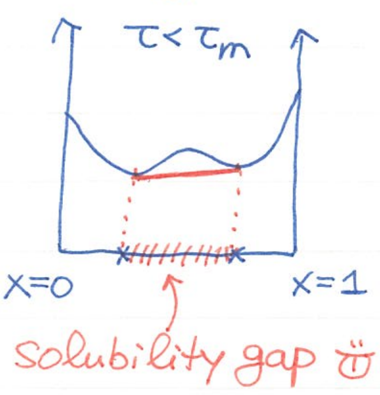
Combine both terms together, the free energy takes the following form,

$$\boxed{f(x) = \Delta\left(-3x^2 - 12x + 9\right) + \tau\left[x\log x + (1-x)\log(1-x)\right]}$$

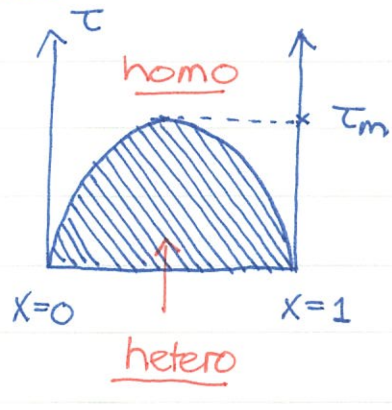
Compute the second derivative,

$$\frac{d^2 f}{dx^2} = -6\Delta + \frac{1}{x(1-x)}\,\tau \leq 0 \longrightarrow -6\Delta + 4\tau_m = 0,\quad \tau_m = \frac{3}{2}\Delta$$

For $\tau > \tau_m$, $d^2f/dx^2 > 0 \longrightarrow$ no solubility gap. For $\tau < \tau_m$, some regime shows heterogeneous mixture.



The phase diagram can be constructed as show on the R.

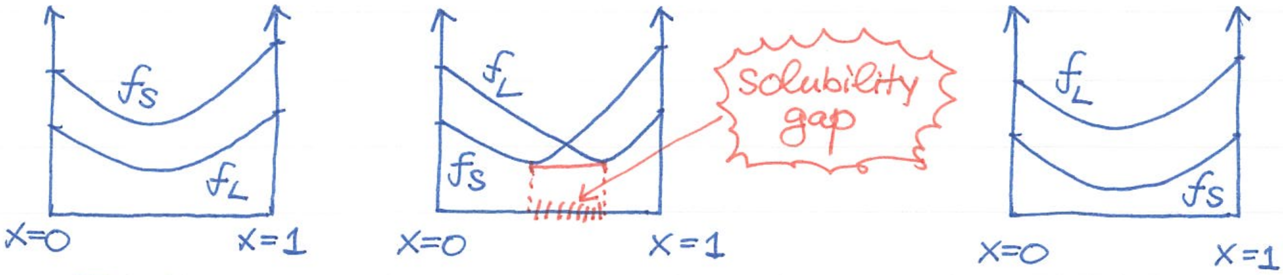


2. Solidification of a binary alloy Consider the binary alloy $A_{1-x}B_x$ with solidification temperature $\tau_A > \tau_B$.

(1) $\tau > \tau_A$: both are liquids $\longrightarrow$ HOMO phases.

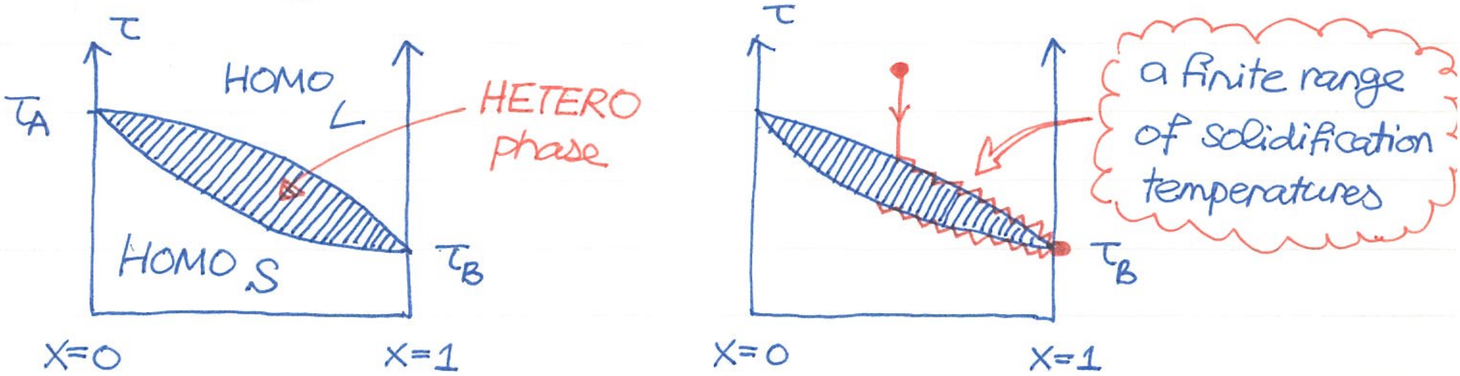
(3) $\tau < \tau_B$: both are solids

Sketch the free energies in these regimes:



$\tau > \tau_A$ $\qquad$ $\tau_B < \tau < \tau_A$ $\qquad$ $\tau < \tau_B$

Collecting the free-energy profiles together, we can cook up the phase diagram.



3. Minimum conductivity in semiconductor

(a) Because $n_e n_h = n_c n_v e^{-\varepsilon_g/\tau} \equiv n_i^2$. In an intrinsic S.C., $n_e = n_h$.

$\longrightarrow$ $n_e = n_h = n_i$ The intrinsic conductivity $\boxed{\sigma_{int} = e n_i (\tilde{\mu}_e + \tilde{\mu}_h)}$

(b) Make use of $n_e n_h = n_i^2$ again.

$$\sigma(n_e) = e\tilde{\mu}_e \left(n_e + \frac{\tilde{\mu}_h}{\tilde{\mu}_e} n_i^2 \cdot \frac{1}{n_e} \right) \longrightarrow \frac{d\sigma}{dn_e} = 0 \quad 1 - \frac{\tilde{\mu}_h}{\tilde{\mu}_e}\frac{n_i^2}{n_e^2} = 0$$

The electron and hole concentrations for σ_{min} are

$$n_e = \sqrt{\frac{\tilde{\mu}_h}{\tilde{\mu}_e}}\, n_i < n_i \,, \quad n_h = \sqrt{\frac{\tilde{\mu}_e}{\tilde{\mu}_h}}\, n_i > n_i \quad \text{because } \tilde{\mu}_e > \tilde{\mu}_h .$$

Finally, the minimum conductivity is

$$\boxed{\sigma_{min} = 2 e n_i \sqrt{\tilde{\mu}_e \tilde{\mu}_h} < e n_i (\tilde{\mu}_e + \tilde{\mu}_h) = \sigma_{int}}$$

4. Potential profile in p-n junction

Solving the Poisson eq. $\frac{d^2\varphi}{dx^2} = -\frac{1}{\epsilon}\rho(x)$ piecewise, the electrostatic potential is

$$\boxed{\varphi(x) = \begin{cases} -V_{bi}, & x > w_p \\ \frac{en_a}{2\epsilon}(x-w_p)^2 - V_{bi}, & 0 < x < w_p \\ -\frac{en_d}{2\epsilon}(x+w_n)^2, & -w_n < x < 0 \\ 0, & x < -w_n \end{cases}}$$

$\varphi(-\infty) \equiv 0$

$\varphi(\infty) = -V_{bi}$

Now one needs to match boundary conditions at $x=0$.

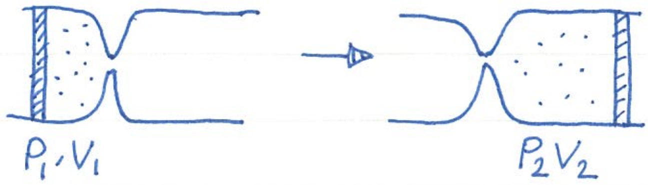
(i) φ is continuous $\quad \frac{en_a}{2\epsilon}w_p^2 - V_{bi} = -\frac{en_d}{2\epsilon}w_n^2$

(ii) $\frac{d\varphi}{dx}$ is continuous $\quad E(0) = \frac{en_a}{\epsilon}w_p = \frac{en_d}{\epsilon}w_n$

Combine (i) & (ii) together, it is easy to find $E(0)$:

$$\boxed{E(0) = \sqrt{\frac{2e}{\epsilon}\frac{n_a n_d}{n_a+n_d}V_{bi}} \propto \sqrt{V_{bi}}}$$

5. Joule-Thomson effect



Since there is no heat transfer involved,

$$\Delta U = \cancel{Q} + W \longrightarrow U_2 - U_1 = P_1V_1 - P_2V_2 \quad \text{i.e. } H = \text{const.}$$

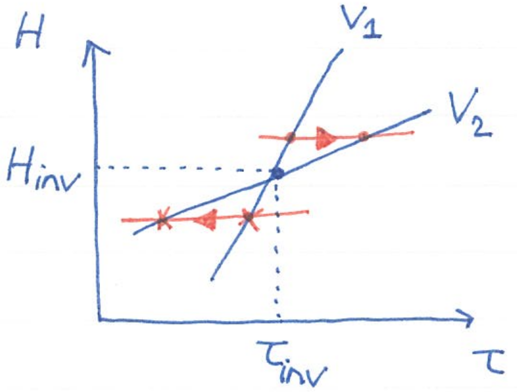
For ideal gas, $H = U + PV = \frac{5}{2}N\tau$ independent of volume change. Thus, the Joule-Thomson effect is absent.

For a van der Waals gas, $PV \approx \frac{N^2}{V}(b\tau - a) + N\tau$

$$H = U + PV \approx \frac{3}{2}N\tau - \frac{N^2}{V}a + N\tau + \frac{N^2}{V}(b\tau - a)$$

$H = \frac{5}{2} N\tau + \frac{N^2}{V}(b\tau - 2a)$ Introduce $\tau_{inv} = \frac{2a}{b}$, the enthalpy can be written in the suggestive form:

$$\boxed{H = \left(\frac{5}{2}N + \frac{N^2 b}{V}\right)(\tau - \tau_{inv}) + \frac{5}{2}N\tau_{inv}}$$

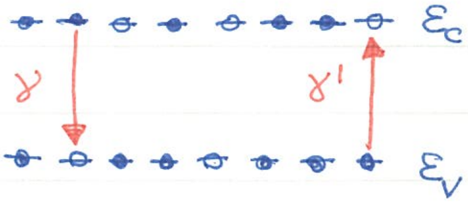


It's clear from the figure

(i) $\tau < \tau_{inv}$, expansion from $V_1 \to V_2$ leads to temperature drop.

(ii) $\tau > \tau_{inv}$, expansion from $V_1 \to V_2$ heats up the gas ☺

6. Recombination of electrons and holes



$$\begin{cases} \text{Probability of an occupied } \varepsilon_c \text{ orbital} = \frac{N_e}{N_c} \\ \text{Probability of an empty } \varepsilon_v \text{ orbital} = \frac{N_h}{N_v} \end{cases}$$

$$R_{c\to v} = \sum \gamma_{c\to v} = N_c N_v \left(\frac{N_e}{N_c} \cdot \frac{N_h}{N_v} \cdot \gamma\right) = N_e N_h \gamma$$

Similarly, the rate for inverse processes is

$$R_{v\to c} = \sum \gamma_{v\to c} = N_c N_v \left[\left(1 - \frac{N_h}{N_v}\right)\left(1 - \frac{N_e}{N_c}\right)\gamma'\right]$$

$$\longrightarrow \quad R_{v\to c} = (N_c - N_e)(N_v - N_h)\gamma'$$

The relation between γ and γ' can be found by detail balance in thermal equilibrium.

$$(R_{c\to v} - R_{v\to c})_{eq} = 0 \longrightarrow (N_e N_h)_{eq}\gamma = [(N_c - N_e)(N_v - N_h)]_{eq}\gamma'$$

$$\boxed{\frac{\gamma'}{\gamma} = \left[\frac{N_e}{N_c - N_e} \, \frac{N_h}{N_v - N_h}\right]_{eq}}$$

← N_e, N_h follow quantum statistics ☺

$$N_e = \frac{N_c}{e^{(\varepsilon_c-\mu)/\tau}+1}\ , \quad N_h = N_v\left[1-\frac{1}{e^{(\varepsilon_v-\mu)/\tau}+1}\right] = \frac{N_v}{e^{(\mu-\varepsilon_v)/\tau}+1}$$

The tunneling rate ratio can be computed,

$$\frac{\gamma'}{\gamma} = \frac{\cancel{N_c}\ 1/\cancel{e^{(\varepsilon_c-\mu)/\tau}+1}}{\cancel{N_c}\ e^{(\varepsilon_c-\mu)/\tau}/\cancel{e^{(\varepsilon_c-\mu)/\tau}+1}} \cdot \frac{\cancel{N_v}\ 1/\cancel{e^{(\mu-\varepsilon_v)/\tau}+1}}{\cancel{N_v}\ e^{(\mu-\varepsilon_v)/\tau}/\cancel{e^{(\mu-\varepsilon_v)/\tau}+1}}$$

$$= e^{-(\varepsilon_c-\mu)/\tau}\, e^{-(\mu-\varepsilon_v)/\tau} = e^{-(\varepsilon_c-\varepsilon_v)/\tau}.$$

The recombination rate is

$$\boxed{R = R_{c\to v} - R_{v\to c} = \gamma\left[N_e N_h - (N_c-N_e)(N_v-N_h)\, e^{-\varepsilon_g/\tau}\right]}$$

where the band gap $\varepsilon_g \equiv \varepsilon_c - \varepsilon_v$.

2012.0505
清大東院