ATS 620
Fall 2011
Problem Set #6
Due 21 October 2011 at 12 PM

1. (10 points) In class, we derived an expression for ΔE^* for heterogeneous ice nucleation on a planar substrate.

   a) Using that expression, plot values of ΔE^* over the range of contact angles $\theta = 0^\circ \rightarrow 180^\circ$ for elastic strain ε=0.0, 0.01, and 0.02. Use the following values:

   $C = 1.7\text{x}10^{10}$ J m^{-3}
   $n_s = 3.07\text{x}10^{28}$ m^{-3}
   $\sigma_{sv} = 0.109$ J m^{-2}
   $T = 263.15$ K
   $k = 1.3087\text{x}10^{-23}$ J K^{-1}
   $e/e_s = 1.1$

   See Figure

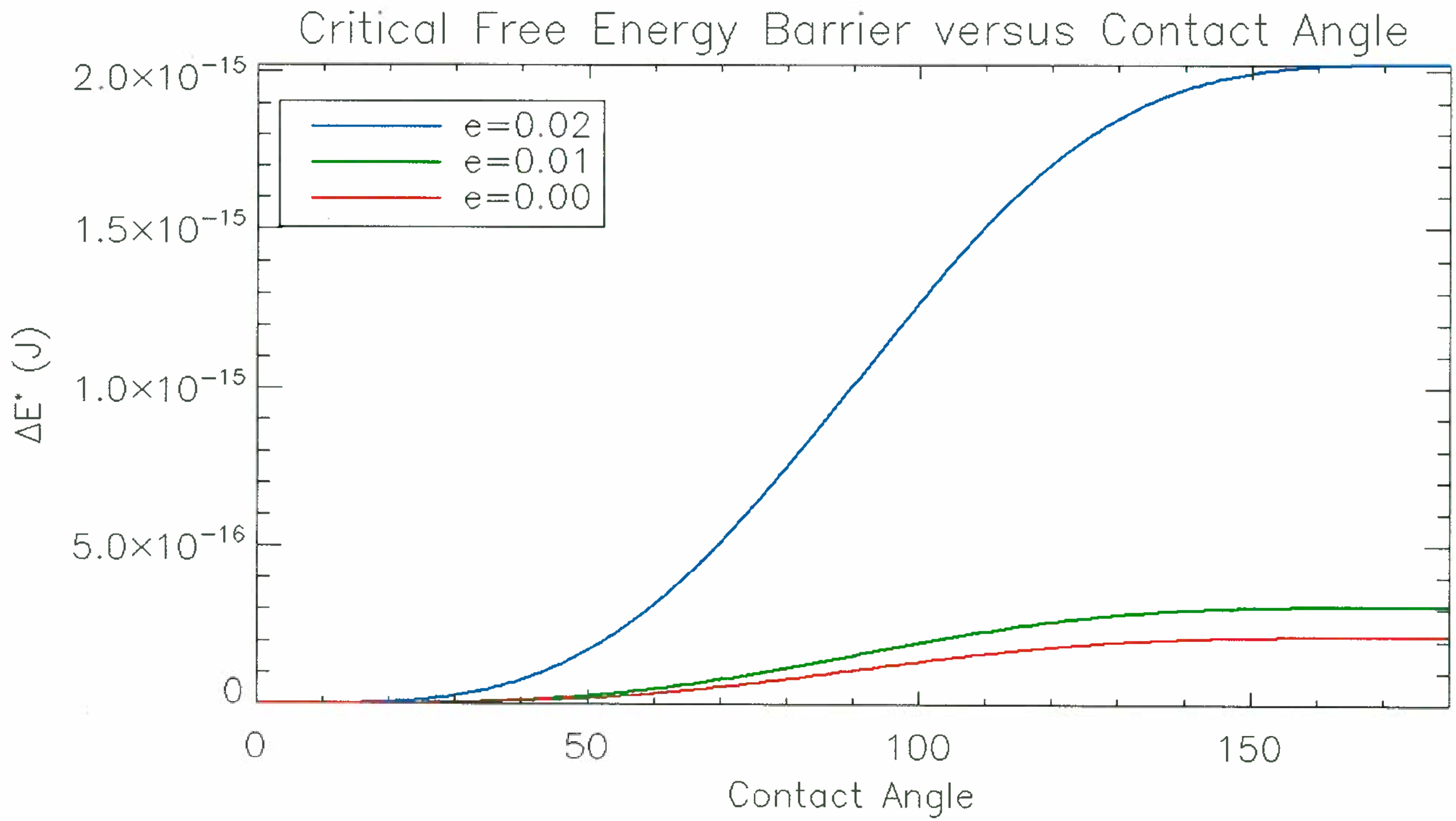
   b) How do variations in contact angle and elastic strain affect the critical energy barrier? Physically, why should you expect this?

① As contact angle increases, ΔE^* increases nonlinearly
② As strain increases, ΔE^* increases nonlinearly

Explanations

① As contact angle increases, the dislocation between the ice lattice and the substrate acts to increase σ_{cs}, which increases $f(m)$ and $\therefore$ ΔE^* increases.

② As elastic strain increases, the substrate looks less like ice. This puts "strain" on the bonds and acts to increase μ_s. This increases ΔE^*


Critical Free Energy Barrier versus Contact Angle
e=0.02
e=0.01
e=0.00
ΔE* (J)
2.0×10^-15
1.5×10^-15
1.0×10^-15
5.0×10^-16
0
0
50
100
150
Contact Angle

2. (10 points) Show the derivation of the equality

$$\Delta\mu = \mu_L - \mu_s = \boxed{RT\ln\frac{e_s}{e_i}} = \boxed{l_f\frac{\Delta T_s}{T_0}}$$

3 4

Term 3 – Supersat Term

Term 4 – Supercool Term

Interpret the meaning of the third and fourth terms, particularly with respect to nucleation.

For Term 3, assume supersaturation is dominant and we have no supercooling

$\boxed{\text{Term 3}}$

Begin with Gibbs free energy,

$$dg = -S\,dT + v\,dp = d\mu$$

dT =0 for constant T

$$d\mu = v\,dp$$

$$d\mu = d(\mu_L - \mu_S) = (v_L - v_S)\,dp$$

☆ Unlike when we did this for equilibrium with water/vapor, we cannot assume $v_L >> v_S$ but we can still assume $v_L << v_v$ and $v_S << v_v$

$$d\mu = d\left((\mu_L - \mu_v) - (\mu_S - \mu_v)\right)$$

Use ideal gas, $d\mu = d(\mu_L - \mu_v) - d(\mu_S - \mu_v) = (\underset{0}{v_L} - v_v)\,dp - (\underset{0}{v_S} - v_v)\,dp$

$$\hookrightarrow\ d(\mu_L - \mu_v) = -v_v\,dp = -\int_{e_s}^{e} RT\,d\ln e = -RT\ln\left(\frac{e}{e_s}\right)$$

$$d(\mu_S - \mu_v) = -v_v\,dp = -\int_{e_i}^{e} RT\,d\ln e = -RT\ln\left(\frac{e}{e_i}\right)$$

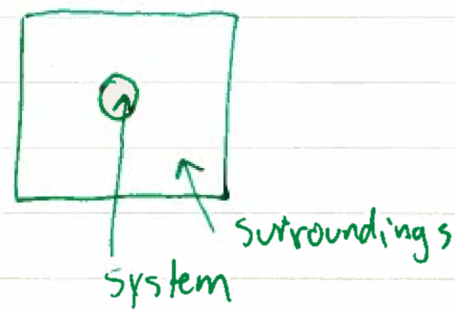
$$d\mu = d\left((\mu_L - \mu_v) - (\mu_S - \mu_v)\right) = d(\mu_L - \mu_S) = -RT\ln\left(\frac{e}{e_s}\right) - \left(-RT\ln\left(\frac{e}{e_i}\right)\right)$$

$$d\mu = RT\left(\ln\frac{e}{e_i} - \ln\frac{e}{e_s}\right) = \boxed{RT\ln\left(\frac{e_s}{e_i}\right)}\ \text{Term 3}$$

Term 4

★ From First Law of Thermo → $Q_{in} = Q_{out}$

Consider a system with a supercooled drop in an environment



For a drop that is supercooled, lets assume the change in chemical potential is purely due to supercooling and not supersaturation, ie.

$$\mu_L - \mu_S = \mu = -s\,dT + \underbrace{v\,dp}_{0} = -s\,dT$$

$$d\mu_{LS} = -\underbrace{(s_L - s_s)}_{\text{This is the change in entropy of the freezing supercooled drop}}dT$$

Going back to HW#1 P3, we need to calculate ΔS of the universe and break our irreversible process into reversible processes.

For drop: $\Delta s = \Delta s_{\text{warming}} + \Delta s_{\text{freezing}} + \Delta s_{\text{cooling}}$

$$= \int_{T_s}^{T_0} \frac{dQ_{rev}}{T} + \frac{L_f}{T} + \int_{T_0}^{T_s} \frac{dQ_{rev}}{T}$$

But, $\Delta S_{univers} = \Delta s_{system} + \Delta s_{surroundings}$ & $Q_{in} = Q_{out}$

We can now write our ΔS for drop as:

$$\Delta S_{system} = \int_{T_s}^{T_o} \frac{dQ_{in}}{T} + \frac{L_f}{T} + \int_{T_o}^{T_s} \frac{dQ_{out}}{T}$$

$+$ — Warming water — cooling of ice

$$\Delta S_{surroundings} = \int_{T_s}^{T_o} \frac{dQ_{out}}{T} + \int_{T_o}^{T_s} \frac{dQ_{in}}{T}$$

Using $|Q_{in}| = |Q_{out}|$ or $Q_{in} = -Q_{out}$, we have

$$\Delta S_{universe}\Big]_L^S = \frac{L_f}{T_o}$$

; but b/c we are going from liq to ice this must be negative.

Plugging this back into our $\Delta\mu$ equation and remembering this process happened in a T_o to T_s range,

$$d\mu = -\Delta S \, dT$$

$$\int_{\mu_S}^{\mu_L} d\mu = \frac{L_f}{T_o} \int_{T_s}^{T_o} dT$$

$$\boxed{\Delta\mu = \mu_L - \mu_S = L_f \frac{\Delta T_s}{T_o} \qquad \text{where } T_s \equiv T_o - T_s}$$

3. (10 points) Problem 9.1 in Rogers and Yau:

An ice crystal in the form of a thin hexagonal plate grows by diffusion in an environment saturated with respect to water at a temperature of -4 °C and a pressure of 80 kPa. Determine the time required for it to grow to a diameter of 1 mm, starting from a mass of 10^{-8} g. Take the capacity to be that of the circumscribing disk. Assume that the mass and the diameter of the plate are related by $m=1.9\times10^{-2} D^3$, with mass in g and D in cm. Neglect ventilation effects. If diameter and fall speed are related by $u = xD$, where $x = 520\ s^{-1}$, determine the distance the crystal falls during the growth to 1 mm diameter.

$$\frac{dm}{dt} = \frac{4\pi C(S_i-1)}{\underbrace{\left(\frac{L_s}{KT}\left[\frac{L_s}{R_vT}-1\right]\right]}_{A} + \underbrace{\frac{R_vT}{e_i(T)D_v}}_{B}} \quad (1) \qquad ; \qquad m = 1.9\times10^{-2}D^3$$

$$\frac{dm(t)}{dt} = (3)(1.9\times10^{-2})D(t)^2\frac{dD(t)}{dt} \quad (2)$$

Equate (1) and (2) and using $C = \frac{D}{\pi}$

$$\frac{dD}{dt} = \left(\frac{1}{D^2(3)(1.9e^{-2})}\right)\left(\frac{4D(S_i-1)}{A+B}\right)$$

$$D\frac{dD}{dt} = \underbrace{\frac{4}{(3)(1.9e-2)}\left(\frac{S_i-1}{A+B}\right)}_{Bob}$$

Integrate, $\int_{D_i}^{D_f} D\,dD = Bob\int_{t_i}^{t_f} dt \Rightarrow \frac{D_f^2 - D_i^2}{2} = Bob\,\Delta t$

$$\Delta t = \frac{D_f^2 - D_i^2}{(2)\,Bob}$$

$D_i = 8.07388\times10^{-5}$ m (from m/D relation) ; $D_f = 1.0\times10^{-3}$ m

$$\Delta t = \frac{9.93481\times10^{-7}\ m^2}{(2)(6.7360685\times10^{9}\ m^2 s^{-1})} = \boxed{3624.0 \text{ seconds} = 55.77 \text{ min}}$$

$\Delta H = V_0 T + \frac{1}{2}aT^2$; $V_0 = (520\ s^{-1})(8.07388\times10^{-5}\ m) = 0.04198\ m\,s^{-1}$

$a = 520\frac{dD}{dt} = \frac{du}{dt} = (520\ s^{-1})\left(\frac{D_f - D_i}{\Delta t}\right) = 1.3e{-4}\ \frac{m}{s^2}$

$T = 3624$ sec

$$\boxed{\Delta H = 1.018\ km}$$

4. (20 points) Using your programming language of choice, recreate the axes and isolines from slide 12 of Lecture 20. You do not need to turn in your code, however please turn in both your plot and the equations you used to create the plot.

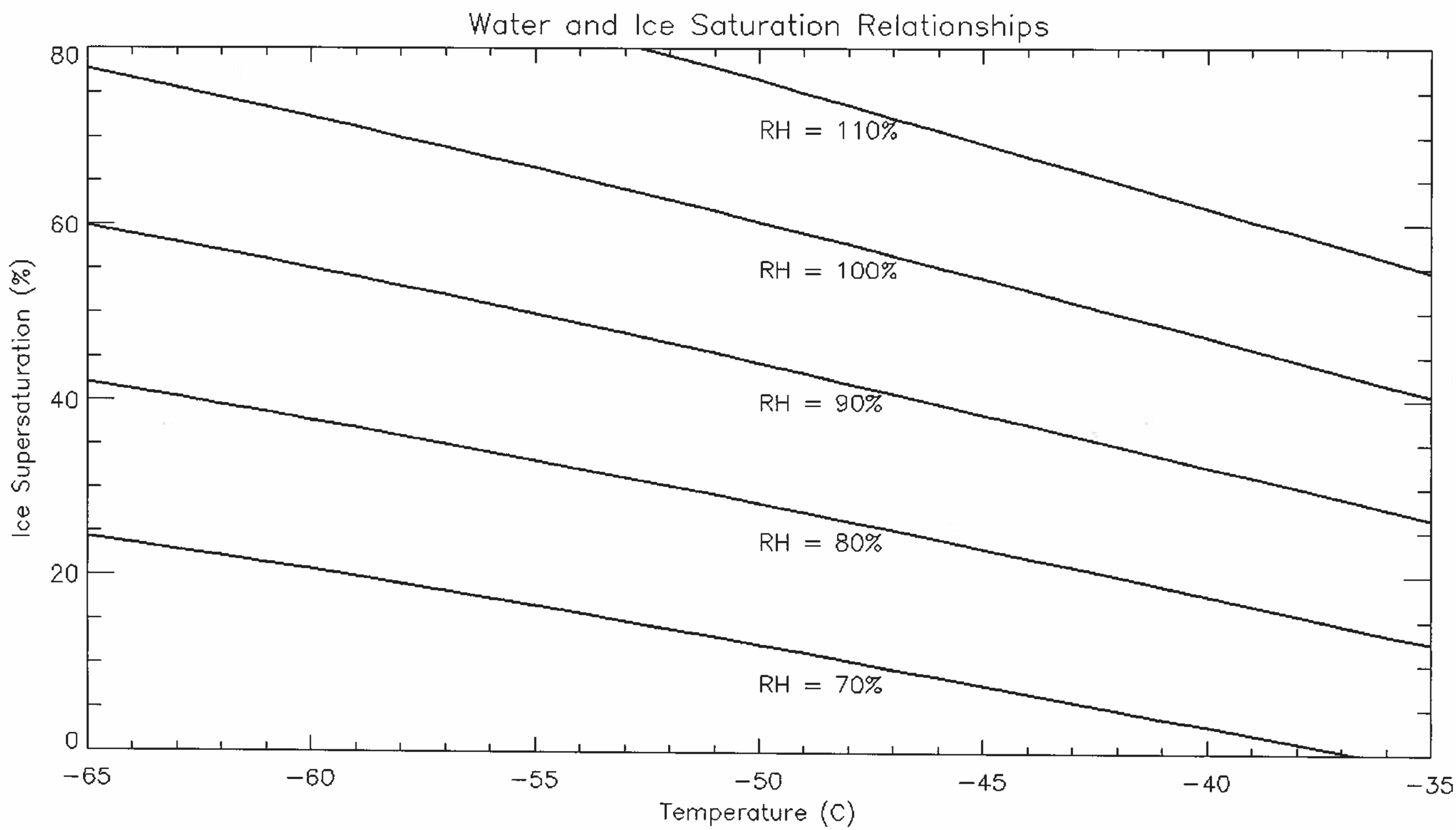
Additional information: the vapor pressures over supercooled water and ice have remained uncertain. Extrapolations from values near the triple point are not accurate, even those in common usgae in the community. Recently Murphy and Koop (2005; paper posted on our class website) reviewed available thermodynamic data, uncovered problems with existing parameterizations, and presented new, more accurate parameterizations for supercooled water and ice vapor pressures. You should use these relationships in solving this problem (and in any other work you do in the below-0 C regime!).

See Plot

Equations used: From M&K (2005)

- Eqn (10) P_{liq}
- Eqn (7) P_{ice}

$$RH_{ice} = RH_w \frac{e_s(T)}{e_i(T)}$$


Water and Ice Saturation Relationships
RH = 110%
RH = 100%
RH = 90%
RH = 80%
RH = 70%
Ice Supersaturation (%)
80
60
40
20
0
−65
−60
−55
−50
−45
−40
−35
Temperature (C)