02_Cloud Seeding

Overview

Cloud seeding is a rain-maker from clouds that do not spontaneously evolve into water droplets. The seeding helps to "nucleate" water droplets that grow into a rain.

The seeding is promoted by spraying small crystals of potassium iodide into the clouds. The embryos nucleate on the surfaces of the crystals.

We will address two questions:

i. Why do clouds sometimes rain and sometimes not? Why is the rain more likely when the clouds rise higher, when going over the mountains, where the temperature is lower?

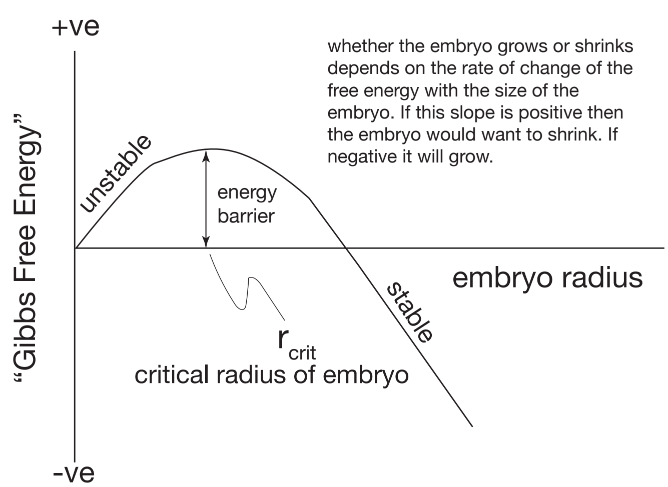
ii. Why do potassium iodide crystals precipitate the water droplets?

The spontaneous nucleation of droplets is called homogeneous nucleation, the surface activated phenomenon is heterogeneous nucleation.

Our objective is to analyze the difference between homogeneous and heterogeneous nucleation.

Relevance to NS&E

The stability of embryos of the condensed phase (water in the present case) depends on their size, as shown below:



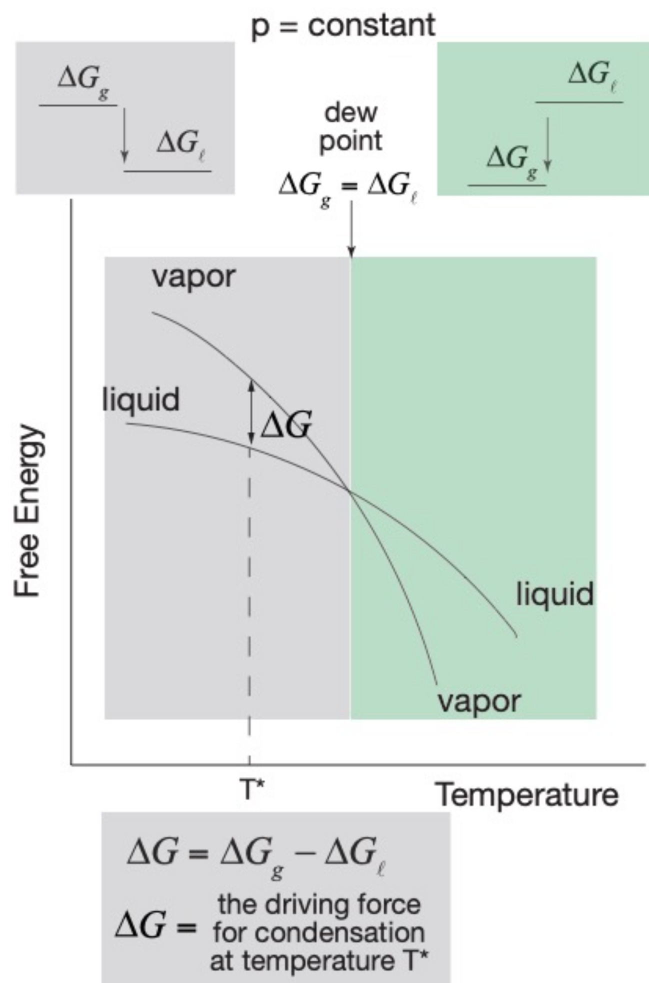
The problem is related to NS&E because the critical size of the nucleus is typically a few nanometers (1 to ~5 nm). Measured in terms of the number of atoms (or molecules as in water) it is about 1000 to 10,000 units within the embryo. The discussion centers on (i) What is Gibbs Free Energy? and (ii) What is the origin of the critical size?

Gibbs Free Energy

Concepts in physics, chemistry, mechanics and materials science are rooted in "Energy". Gibbs Free Energy is a special version of Energy that is ever present in Materials and Nano Science. It is a thermodynamic quantity that depends only on the "state" of matter; it is not time dependent. For example, in the cloud seeding context, there two states of H_2O, vapor state and the liquid state. Each State has its own Free Energy. The state with the lower value is more stable. The relative stability of vapor and water depends on temperature and pressure, since the Free Energy is a function of these parameters. The relative Free Energy is given the symbol ΔG.

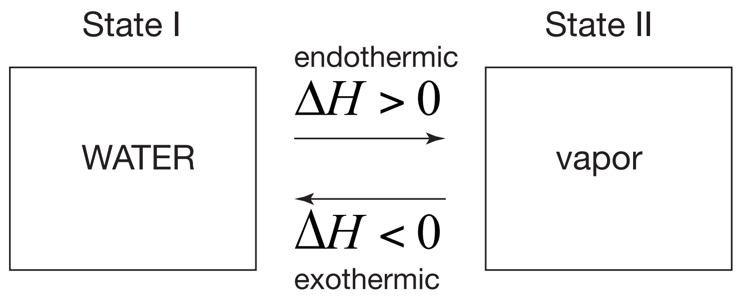
Notes:

• ΔG has units of J per unit volume (J per mol is also used, but here we shall consider per unit volume)



Concepts of Enthalpy and Entropy (the driving force for condensation)

$$\Delta G = \Delta H - T\Delta S$$



$$\Delta S > 0$$

Therefore at the dew point (DP)*

$$\Delta G = 0$$

$$T_{DP}\Delta S = \Delta H$$

$$\Delta S = \frac{\Delta H}{T_{DP}}$$

*DP is defined as the temperature where the vapor pressure of water becomes equal to the atmospheric pressure

Estimate the driving force below the dew point for condensation:

At equilibrium we have that

$$\Delta S = \frac{\Delta H}{T_{DP}}$$

$$\Delta G(T^*) = \Delta H - T^*\Delta S$$

$$\Delta G(T^*) = \Delta H - T^*\frac{\Delta H}{T_{DP}}$$

$$\Delta G(T^*) = \Delta H\left(1 - \frac{T^*}{T_{DP}}\right) = \Delta H\frac{T_{DP} - T^*}{T_{DP}} = \Delta H\frac{\Delta T_{supercool}}{T_{DP}}$$

Units:

ΔH has units of J mol^{-1}, J m^{-3}

ΔG also has units of J mol^{-1}, J m^{-3}

Let us think about analysis for the stability of the embryo as a function of its size:

The volumetric driving force for nucleation = $\Delta G_{embryo} = \Delta G(T^{*})\left[\text{volume of the embryo}\right]$ (1)

This is a negative quantity.

Equation (1) is favoring nucleation and growth of an embryo.

What is opposing the formation of the embryo?

It is the higher energy of the atoms on the surface (as compared to within) that are opposed to nucleation!

The surface opposition to nucleation is formally written in the following way,

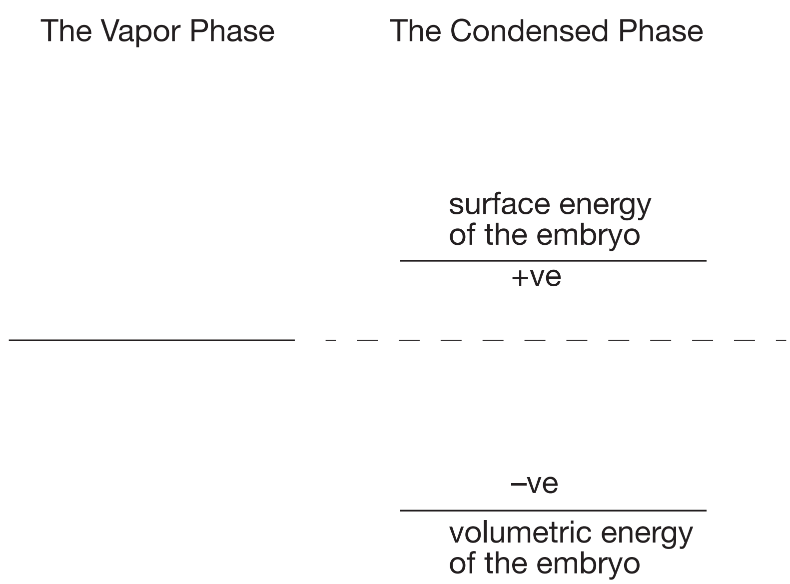
(surface area of the embryo)x(a quantity that represent the higher energy of the atoms on the surface)

This quantity can be expressed as surface energy, that is the excess energy of the atoms on the surface relative to those within the nucleus. (Conceptually it will be equal tot higher energy of one atom on the surface -relative to the bulk- multiplied by the number of atom per unit area of the surface).

γ_S is called the surface energy and it has units of J m^{-2}.

The surface energy of the embryo is positive because it is opposed to nucleation.

This positive quantity in the transformation energy = γ_S *(surface are of the embryo) (2)



Therefore the total energy of the embryo relative to the vapor state is:

$$\Delta G_{embryo} = -\Delta G(T^{*}) * \frac{4}{3}\pi r^{3} + \gamma_S * 4\pi r^{2} \quad (3)$$

The writing of Eq. (3) requires that γ_S is also a free energy parameters.

Plotting Eq. (3) will show a maximum which is the critical size of the embryo for its spontaneous growth.

The answer would be

$$r^* = \frac{2\gamma_S}{\Delta G(T^*)} \qquad (3)$$

The height of the free energy barrier

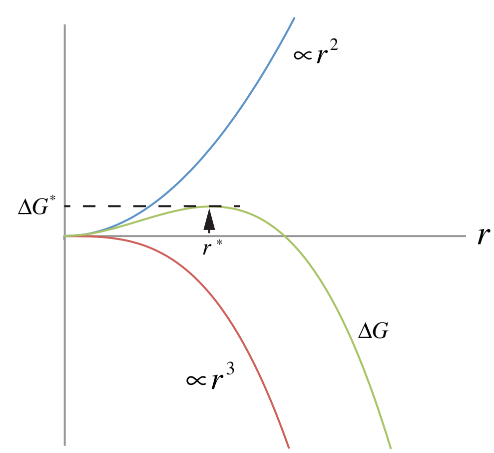
$$\Delta G^{\bullet} = \frac{\Delta G(T^*)\left(\frac{4}{3}\pi r^{*3}\right)}{2} \qquad (4)$$

This is homogeneous nucleation!!

Derivation of Eq. (4)

Starting point:

$$\Delta G_{embryo} = -\Delta G(T^*) * \frac{4}{3}\pi r^3 + \gamma_S * 4\pi r^2 \qquad \text{(Eqn 3)}$$



$$\Delta G_{embryo} = -\Delta G(T^*) * \frac{4}{3}\pi r^3 + \gamma_S * 4\pi r^2$$

$$\frac{d\Delta G_{embryo}}{dr} = -\Delta G(T^*) * 4\pi r^2 + \gamma_S * 8\pi r = 0$$

$$r* = \frac{2\gamma_S}{\Delta G(T^*)}$$

$$\Delta G^*_{embryo} = -\Delta G(T^*) V * + \frac{2}{\Delta G(T^*)} \frac{\Delta G(T^*)}{2} \gamma_S * 4\pi r *^2$$

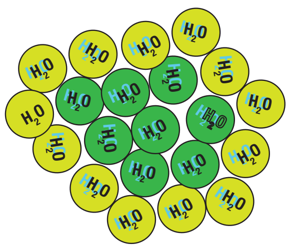
$$\Delta G^*_{embryo} = -\Delta G(T^*) V * + \frac{\Delta G(T^*)}{2} * 4\pi r *^3 \frac{3}{3}$$

$$\Delta G^*_{embryo} = -\Delta G(T^*) V * + \frac{3}{2}\Delta G(T^*) V * = \frac{\Delta G(T^*) V *}{2}$$

Notes:

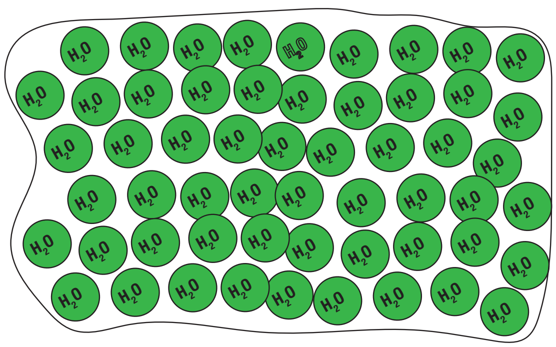
The derivation of r * and delta G embryo star are very general. These are therefore "powerful" results although the analysis is utterly simple. $r* = \frac{2\gamma_S}{\Delta G(T^*)}$; $\Delta G^*_{embryo} = \frac{\Delta G(T^*) V *}{2}$.

Figures used during class today:



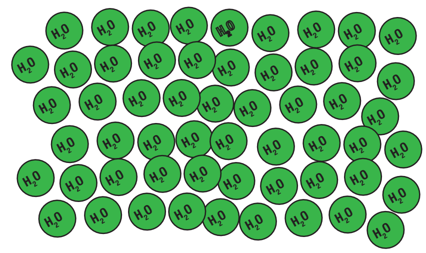
yellow: surface
green: bulk

Embryo

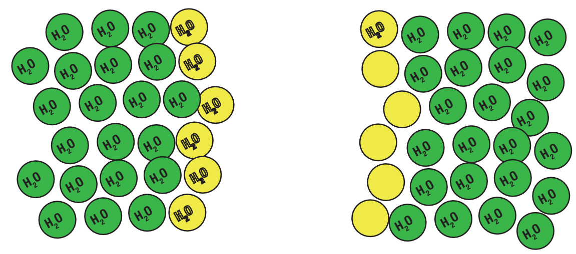


Atoms within Bulk

State I



State II



$\Delta G_S = G_{II} - G_I$ = energy of the molecules on the surface relative to their energy within the bulk

$= 2\gamma_S$

where γ_S is the excess energy per unit area of the surface.

Left: The embryo consists of two types of atoms (or molecules): those that lie within its volume and those that lie on its surface. The surface atoms have a higher energy than the "volume" atoms. The latter are the same as within water surrounded by other water molecules. However the surface atoms (shown in yellow) have higher free energy than the atoms within the embryo. The energy of the atoms within the embryo is written as energy per unit volume times the volume of the embryo.

Right: The energy of the atoms on the surface is prescribed by the energy (the Free Energy) of single atoms multiplied by the number of atoms per units area which gives rise to the quantity called surface energy (which has units of J m^{-2}).