9. Surface Thermodynamics and Nucleation of Water Droplets and Ice Crystals

Sources:

My old class notes **Rogers and Yau, Ch. 6** Wallace and Hobbs, Ch. 4 Pruppacher and Klett (1978), Ch. 5,6,7; Warneck (1988)

Question: What physical processes promote the formation of cloud droplets and ice crystals within warm and cold clouds?

9.1 Thermodynamics of surfaces

9.1.1 Review of Gibbs and Helmholtz free energy

In Chapter 4 we defined the Gibbs free energy, g, and the Helmholtz free energy, f, which assist in the definition of equilibrium conditions for water phase change processes considered in this chapter. Expressions for f and g, along with their differentials are:

f = u - Ts. $df = du - Tds - sdT = -sdT - pd\alpha$ $g = u - Ts + p\alpha \quad [=u+f]$ $dg = du - Tds - sdT + pd\alpha + \alpha dp = -sdT + \alpha dp.$

For a phase change we need to consider two additional terms in the Gibbs free energy, one related to changes in chemical potential (associated with phase change) and a second related to work connected to the formation of a physical surface (i.e., a discontinuity).

9.1.2 Background

Up to this point we have considered thermodynamics in terms of bulk properties (e.g., p, T, ρ , r_v, etc). In clouds, the liquid and solid water substance is distributed (dispersed) as small particles that have large surface to volume ratio. Also, phases in direct contact are separated by thin transition regions only a few molecules thick (and hence they can be considered geometric surfaces). These properties necessitate a consideration of such surface effects (fortunately, in terms of macroscopic thermodynamics) when considering phase equilibria and the nucleation of water (and ice) particles in clouds.

When the area of an interface such as the surface of a liquid and its vapor is increased, molecules from the interior have to be brought to the surface. In this process work must be done against the cohesive forces in the liquid. The molecules in the interior are surrounded on all sides by adjacent molecules, while those at the surface have neighbors of the same phase only on "three" sides (i.e, there is an asymmetry). The *surface tension* is defined as the work per unit area (A) done in extending the surface of the liquid. It has units of energy per unit area. The surface energy is increased by an amount equivalent to the work done (it takes work to expand a water droplet), so the surface tension may be written as

$$\sigma = \partial g / \partial A.$$

Some careful thought on the previous statements would suggest that the First Law applies here, since work and energy are involved. This is, in fact, the reason why we introduce the Gibbs free energy as a tool to examine this problem.

9.1.3 Surface energy and surface free energy

When the effects of surfaces are included, the Gibbs function takes on two additional terms related to the additional energy and work alluded to in the previous section:

where s is entropy, n_i is the number of moles of the ith component, and μ represents the chemical potential (at the surface), which is the Gibbs free energy per molecule. Recall from Chapter 3 (Notes, p. 3) that a preliminary form of the First Law,

$$q = \Delta u + \sum e_i$$
,

contained the second term on the RHS, $\sum e_i$, that was related to the work of expansion *plus* other forms of work, such as last two terms on the RHS of Eq. (9.1). (If you recall, I promised that we would revisit this issue.) The quantity ($\partial g/\partial A$) at constant temperature, pressure and composition is termed the *surface tension* σ . It is a quantity easily measured for liquids. To compute the surface energy one makes use of the Gibbs-Helmholtz equation

 $dg = dh - Tds = dh + T(\partial g/\partial T).$

We will also define h_s, the total surface energy, as

$$h_s = \sigma - T(\partial s / \partial T).$$

The surface tension of water depends on temperature according to the empirical relation

 σ = 76.10 - 0.155T (units: erg cm⁻²; T in °C; recall that 1 J = 10⁷ erg).

A plot of this function is provided on an attached figure (Fig. 5-1 from Pruppacher and Klett, 1973). At 20 °C σ is 72.75 erg cm⁻² and the total surface energy at this temperature is 112 erg cm⁻². The change of surface tension with temperature is always negative, and the surface tension becomes zero at the critical temperature (647 K; see Figs. 5.1-5.3 in Chap 5 of the Notes). Surface tension for pure water can be modified by the presence of dissolved salt such as NaCl. Fig. 5-2 (from Pruppacher and Klett, attached sheet) presents data for sodium chloride (NaCl), (NH₄)₂SO₄ (ammonium sulfate), NH₄Cl (ammonium chloride), and NH₄NO₃ (ammonium nitrate) solutions.

9.1.4 Hydrostatic pressure difference over a curved surface

We will now examine the relation between work of expansion and surface tension. If we increase the radius (virtual displacement) of a spherical bubble of radius r, it is necessary to balance the work of expansion (pdV) by the surface tension, i.e.,

$$pdV = 2\sigma dA$$
.

If the radius is to be increased, then the pressure within the sphere must be greater than the pressure outside, and the above equation can be written as

 $p_i - p_o = 2\sigma(dA/dV) = 4\sigma/r.$ (dA/dV = 2/r for a sphere.)

For a liquid drop (which has one surface or interface) rather than a bubble (which has two interfaces) the pressure difference is

 $\mathbf{p}_{i} - \mathbf{p}_{o} = 2\boldsymbol{\sigma}/\mathbf{r}. \tag{9.2}$

This is a special case of the LaPlace equation

$$p_i - p_o = \sigma(r_1^{-1} + r_2^{-1})$$

where the r's are the principal radii of curvature. For a sphere the two radii are equal. For a flat surface, the radii are infinite and no pressure difference exists. The important aspect of this discussion is that a pressure difference is associated with a curved surface, according to Eq. (9.2). This pressure difference obeys the r⁻¹ relationship.

9.2. Nucleation of cloud droplets (vapor \rightarrow water)

Define: Homogeneous nucleation Heterogeneous nucleation

9.2.1 Homogeneous nucleation

This problem considers the spontaneous formation, through the (improbable) collision of a sufficient number of water vapor molecules, to form an embryonic drop of sufficient size to remain intact. The term "sufficient number" implies a minimum droplet size, which will be defined below. Assume that this droplet has a volume V and surface area A. Let μ_l and μ_v be the chemical potentials for the respective liquid and vapor phases, and n the number of water molecules per unit volume. The change in Gibbs free energy (due to condensation) of the system is

 $nV(\mu_v - \mu_l)$.

From previous considerations regarding surface energy, we have indicated that work is involved in: (a) creating the surface of a droplet, and (b) increasing the volume of an existing droplet. The work involved is $A\sigma$, where σ is the surface tension, or the work required to create a unit area of the vaporliquid interface. This is *not* an equilibrium transformation, that is

 $A\sigma \neq nV(\mu_v-\mu_l).$

Instead, the change in g, (Δg) will differ from the work term according to the following:

 $\Delta g = A\sigma - nV(\mu_v - \mu_l),$

where Δg is the net increase of energy of the system due to the formation of the drop. We have previously determined (Section 5.2, Notes, or Wallace and Hobbs, pp. 101-102) that the change in chemical potential (μ_v - μ_l) can be expressed in terms of bulk thermodynamic quantities (T and relative humidity, or saturation ratio S=e/e_s) as

$$(\mu_v - \mu_l) = kTln(e/e_s).$$

We can then write

$$\Delta g = A\sigma - nVkTln(e/e_s).$$

For a spherical water droplet or radius r, this becomes (using relations for the volume and area of a sphere)

$$\Delta g = 4\pi r^2 \sigma - (4/3)\pi r^3 nkTln(e/e_s). \tag{9.3}$$

We can determine from measurements that the equilibrium vapor pressure over a curved surface exceeds that over a flat surface at the same temperature. (See attached Fig. 4.11 from W&H) Eq. (9.3) is a reflection of this. We need to consider two terms here, the first related to surface effects and the second related to changes in chemical potential. If $e < e_s$ then the second term is positive and Δg grows in a nonlinear fashion as r increases. Since a system approaches an equilibrium state by reducing Δg , the formation of droplets is not likely under subsaturated conditions. However, random collisions of water molecules do produce embryonic droplets that continually form and evaporate in the atmosphere, but these are not visible as cloud droplets. When the air is supersaturated (e.g., by adiabatic ascent/cooling) then $e > e_s$, and the second term is negative. In this case, Δg attains a maximum value at some critical radius R (see attached Fig 4.10 from W&H). We find R by differentiating (9.3), $d(\Delta g)/dr$, and setting the result to zero. Do this yields *Kelvin's formula*:

$$R = 2\sigma / nkTln(e/e_s).$$

Fig 4.10 (W&H) below plots Eq. (1) for positive and negative values of lnS and defines R, the critical radius. The free energy becomes zero when r = (3/2)R. The table below presents some calculations at T=20 °C (compare with Table 6.1 of R&Y).

Table 9.1. The dependence of R and Δg_{max} on the saturation ratio e/e_s .

e/e _s	R (μm)	Δg_{max} (erg)
1.005	2.2x10 ⁻¹	1.42x10 ⁻⁷
1.01	1.1x10 ⁻¹	3.56x10 ⁻⁸
1.02	5.4x10 ⁻² 8.99x10 ⁻⁹	
1.05	2.2x10 ⁻²	1.48x10 ⁻⁹
1.10	1.1x10 ⁻²	3.88x10 ⁻¹⁰
1.50	2.6x10 ⁻³	2.14x10 ⁻¹¹
2.00	1.6x10 ⁻³	7.34x10 ⁻¹²
3.00	9.8x10 ⁻⁴	2.92x10 ⁻¹²
4.00	7.8x10 ⁻⁴	1.86x10 ⁻¹²

(9.4)

We can consider Δg_{max} as a free energy barrier which must be overcome to permit the formation of a droplet which will grow. At values greater than R, Δg is negative and a droplet in this size range will grow spontaneously. For sizes less than R, droplets will not grow spontaneously. Eq. (2) can be used to calculate the radius R of a droplet that is in (unstable) equilibrium with air at some saturation S = e/e_s. Alternatively, it can be used to determine S over a droplet of specified radius.

9.2.2 Concentration of critical embryos

A critical embryo is defined as a water droplet of radius r=R. To determine the concentration of critical embryos, we utilize the Boltzman relation

$$\frac{n_{\rm R}}{n_{\rm v}} = \exp\left(\frac{-\Delta g_{\rm max}}{kT}\right). \tag{9.5}$$

where n_R is the number of critical embryos per unit volume while n_v is the number of individual water vapor molecules per unit volume. To very good approximation we have assumed that the number of water vapor molecules tied up in the embryos of the various sizes is negligible with respect to the number of water molecules in the vapor phase. From Table 9.2 below we can see that there are essentially no critical embryos in the free atmosphere.

Table 9.2. Number of critical embryos (n_R) of pure water at T=20 °C.

<u>e/e</u> s	<u> </u>	
1.005	0	
1.01	0	
1.10	0	
1.50	0	
2.00	5x10 ⁻⁶¹	
3.00	2x10 ⁻¹³	
4.00	4x10 ⁻²	

9.2.3 Nucleation rate

The nucleation rate is defined as the number per unit volume of supercritical droplets (i.e., droplets with r>R). This rate is given by the product of the critical embryo number concentration n_R and the collision rate at which vapor molecules strike the embryo surface. The collision rate can be determined from the kinetic theory of gases as the number of gas molecules striking a unit area of substance per unit time:

$$v = \frac{e}{(2\pi m kT)^{1/2}}$$
 (9.6)

where e is in mb. For water this reduces to

$$v = 6.21 \times 10^{21} \text{eT}^{-1/2}$$
.

Collision rate is directly proportional to the water vapor pressure (e), a result which may be inituitive (or at least consistent with simple thinking).

The surface area of the critical embryo is $4\pi R^2$ and hence

 $v_c = 7.81 \times 10^{22} R^2 e T^{-1/2}$.

The initial nucleation rate, J, is given by

 $J = n_R v_c$.

This is an initial rate before the supply of water vapor is reduced by droplet formation. An attached table gives J values for the condensation of water at 288 and 273 K as a function of $S=e/e_s$.

What do you conclude?

9.2.4 Homogeneous nucleation of ice (crystals) from water vapor (vapor \rightarrow ice)

This is a deposition process as opposed to a condensation process for the case of water droplets, and thus, the latent heating is greater. As in the water case, the supersaturation ratio with respect to ice is a function of T only, and the same theory described for the case of water applies here. Precise values of the interfacial tension of ice against water do not exist. This value is greater than that of the surface tension of water. If realistic values are used, we again find that even at low temperatures of -60 °C that the critical concentrations are zero (and less than that for vapor-liquid). Thus, homogenous nucleation of ice does not occur in the atmosphere.

9.2.5 Homogeneous nucleation of ice from liquid water (water \rightarrow ice)

This represents the second path that is theoretically available for homogeneous ice nucleation. Here there are two unknowns (I think this is true -- I am paraphrasing from unpublished notes from 1977): (1) The interfacial tension between liquid water and ice is unknown, and (2) a simple theory for collision rates does not exist. We can guess that the interfacial energy for ice-water is in the range 20-30 erg cm-2. (This compares to ~100 erg cm⁻² for ice-vapor and ~73 erg cm⁻².) What we know from laboratory experiments and from in situ cloud measurements is that all (cloud) water is essentially frozen at -40 °C. Thus, homogeneous nucleation from cloud water to ice crystals is likely, but probably not dominant, in cloud systems.

9.2.6 Summary of homogeneous nucleation

We have seen that the only homogeneous nucleation process active in clouds is through the water-ice phase transition. Measurements of S within clouds rarely exceed 1.01 (near cloud base). This implies that homogeneous nucleation does not occur, since the required S for embryonic droplets at radius 0.1 μ m exceeds 1.01. We will now consider the heterogeneous nucleation (of water droplets and ice crystals) which is responsible for the formation of the elemental cloud particles.

9.3 Heterogeneous nucleation of water droplets

We have seen that the formation (homogeneous nucleation) of droplets in a pristine atmosphere is a difficult process requiring appreciable supersaturation. We now turn to the heterogeneous nucleation in which the presence of foreign particles relaxes the constraints of homogeneous nucleation. We will first examine the nature of atmospheric aerosols and then proceed with a general examination of heterogeneous nucleation.

9.3.1 Atmospheric aerosol particles (AP)

Aerosols are comprised of particles which may exist in solid or liquid (excluding water) form. Their concentration and chemical make-up exhibit considerable variability. Aerosol sizes range from $\sim 10^{-4}$ to $\sim 100 \ \mu$ m, and concentrations may range from 10^{-6} to 10^7 cm^{-3} . It is convenient to divide AP into 3 size categories:

Aitken particles ($r < 0.2 \ \mu m$), large particles ($0.2 < r < 2.0 \ \mu m$), giant particles ($r > 2.0 \ \mu m$).

As shown in the Fig 6.3 of R&Y, the smallest AP are most numerous. [This distribution was measured in an interior continental setting near Miles City, Montana.] We also note that Aitken nuclei exist in higher concentrations over continents than over oceans, a facet related to the source region. Over continental areas, AP concentrations drop off sharply with increasing height, indicating that the surface acts as a source. (See Fig. 4.1 from Wallace and Hobbs).

Sources of AP include both natural and man-made (anthropogenic) sources (see Table 4.1 and Fig. 4.7 from Wallace and Hobbs, and reproduced below). A large fraction of Aitken nuclei originates from combustion processes. Other sources include gas-to-particle conversion, wind-blown dust and even extra-terrestrial particles (meteoric debris).

Aerosol sinks include losses on the small end from coagulation, on the large end from sedimentation (fallout), and from scavenging (capture) from cloud droplets and precipitation. This latter process may account for 80% or more of the total mass of aerosols removed from the atmosphere. (CCN, diffusiophoresis, impaction for $r > 2 \mu m$)

As mentioned above, a wide variety of aerosols exist within the atmosphere. Some of these serve as nuclei to promote the formation of (a) water droplets from the vapor, (b) ice crystals from the vapor and (c) ice crystals from water droplets.

9.3.2 Cloud condensation nuclei (CCN)

These are defined as AP which are capable of initiating drop formation at relatively low supersaturation. CCN represent a very small subset of the total AP. CCN concentrations vary from generally low values over oceans (~100 cm⁻³), to high values over continental areas (~600 cm⁻³). The size range encompasses the interval 0.1-1.0 μ m, which is the so-called accumulation mode defined by R&Y on p. 93. The accumulation mode corresponds to the peak in the surface and volume curves of Fig. 6.3. This peak is also seen in Fig. 4.7 from Wallace and Hobbs. Note that the CCN number is a function of supersaturation (S-1), where S = e/e_s. This dependence can be expressed as

$$N_{\rm CCN} = C(S-1)^k \tag{9.7}$$

where C and k are approximately constant but vary considerably as indicated on p. 95 of R&Y. e.g.,

maritime air: 30<C<300 cm⁻³; 0.3<k<1.0, continental air: 300<C<3000 cm⁻³; 0.2<k<2.0.

Thus, CCN at a particular location can exhibit appreciable variation. Over oceans, CCN concentrations are nearly uniform with height as shown in Fig. 9-4 from P&K, in contrast to continental regions which CCN decrease with height (Fig. 4.1 from Wallace and Hobbs). It is estimated that only 1-10% (or less) of all aerosols serve as CCN as shown in the table below.

Table 9.2: Comparison between total concentration of aerosol particles and concentration of cloud condensation nuclei activated at 1% supersaturation at various locations. Taken from Pruppacher and Klett (1978).

Location	Aitken particles (cm ⁻³)	CCN (cm ⁻³)
Washington D.C.	78,000	2000
(Allee, 1970)	68,000	2000
	57,000	5000
	50,000	7000
Long Island, NY	51,000	220
(Twomey and Severynse,	18,000	110
1964)	5,700	30
Yellowstone National Park	1,000	15
(Auer, 1966)		

9.3.3 Nucleation onto water-soluble CCN

- controlled by the mass and chemistry of the water-soluble component
- deliquesence onto hygroscopic particles at RH < 100%

The most efficient CCN are those that are both wettable (or hygroscopic) and water soluble. Such CCN serve as very efficient centers onto which water vapor can condense, with the nucleated hetergeneous drop then attaining a critical size. Salt particles (NaCl - prominent over oceans) and ammonium sulfate particles [(NH₄)₂SO₄ - prominent over continents] are particularly efficient CCN. The aerosols that are soluble in water effectively reduce the saturation required to achieve critical radius. This occurs for the following reason. Since e is proportional to the number of molecules at the surface, we see that if a fraction of water molecules is replaced by the agent being dissolved (an ion), then the fractional change in e is

$$e'/e_s = f = n_0 / (n_0 + n') \approx 1 - n'/n_0$$
 (n'<

where e' is the saturation vapor pressure over a solution droplet containing a kilomole fraction of pure water and e_s is the vapor pressure over a pure water droplet of the same r and T, n_0 and n' are the number of water and solute molecules.

In many solutions, dissolved molecules are dissociated, so (9.8) is modified by the van Hoff factor i (\sim 2). Then

 $n = iN_0M/m_s$ (N₀ - Avogadro's no., M - mass of solute, m_s - molec. weight of solute)

 $n_0 = N_0 m/m_v$ (m - mass of water, m_v - molec. wt. of water)

Since $m = V \times \rho_L = (4/3)\pi r^3 \rho_L$, then (9.8) can be written as

$$e'/e_{s} = 1 - [3im_{v}M/4\pi\rho_{L}m_{s}] r^{-3} = 1 - br^{-3}.$$
(9.9)

From the Kelvin Eq. (9.4) we can write

 $S = e/e_s = \exp[(2\sigma)/(R_v T\rho_L r)] = e^{a/r}.$

For the dissolved substance the above eq. is modified to

 $S = e'/e_s = \exp[(2Mr)/(R_v T\rho_L r)].$

or $e_{s}'(r)/e_{s}(\infty) = [1 - br^{-3}]e^{a/r}$.

For small a/r, $e^{a/r} = 1 + a/r + (a/r)^2/2 + ... \approx 1 + a/r$, we can write $e_s'(r)/e_s(\infty) = (1-br^{-3})(1+a/r)$

$$= 1 - br^{-3} + ar^{-1} - abr^{-4}$$
.

If we ignore the last term of the above equation then (with justification)

$$e_{s}'(r)/e_{s}(\infty) \approx 1 + ar^{-1} - br^{-3}$$
 (9.10)
curvature term

A plot of Eq. (9.10) yields the Kohler curve, an example of which is given in Fig. 4.12 of Wallace and Hobbs (attached) and in Fig. 6.2 of R&Y. Note that for small r the (negative) solute term dominates. Eq. (9.10) can be solved to find the critical radius and corresponding superaturation at the critical radius:

$$r^* = [3b/a]^{1/2};$$
 $S^* = 1 + [4a3/27b]^{1/2}.$ (9.11), (9.12)



Fig. 9.2 Equilibrium saturation ratio of a solution droplet formed on an ammonium sulfate condensation nucleus of mass 10-16 g. Taken from Rogers and Yau (1989, their Fig. 6.2).

Nucleation onto a water-insoluble CCN

Many CCN are a mixture of soluble and insoluble AP. In this case we must consider the effects of the water/solid surface. We can write the Kohler Eq. from the soluble result as

 $\ln (e/e_s) = 1 + a/r - b/(r^3 - r_u^3)$

where r_u is the equivalent radius of the water-insoluble sphere. If we plot the supersaturation required for activation, we find that the initial size needs to be >0.1 μ m.

Nucleation onto a water-insoluble, partially wettable CCN

We will ignore the mathematical development and only mention some research results here. In this case the critical saturation ratio is highly dependent on contact angle, which is defined in Figure 9-6 (attached) from Pruppacher and Klett. It can be shown that CCN under this category are probably not important unless the contact angle is less than 10-15 deg. For example, if we consider that the (S-1) value reached in clouds is typically smaller than 3%, we must require that AP of r>.01 micron have contact angles less than 12 deg. Little is known about actual contact angles for AP. However, available measurements suggest that silicate particles are not likely to serve as CCN.

An aerosol defined as hydrophilic if it has a contact angle of 180°.

In the real atmosphere, actual CCN are composed of a combination of the above due to processes of coagulation, etc.

Figures taken from Wallace and Hobbs

Figures taken from Wallace and Hobbs (continued) Figures taken from Prupacher and Klett Figures taken from Prupacher and Klett (continued)

Homework:

Complete the following from Rogers and Yau: 6.3, 6.10

Appendix

Fig. 9.a. Comparative sizes, concentrations, and terminal fall speeds of particles involved in the "warm"rain process. Based on Fig. 6.1 in Rogers and Yau (1989), who borrowed it from MacDonald (1958).

