Chap. 9

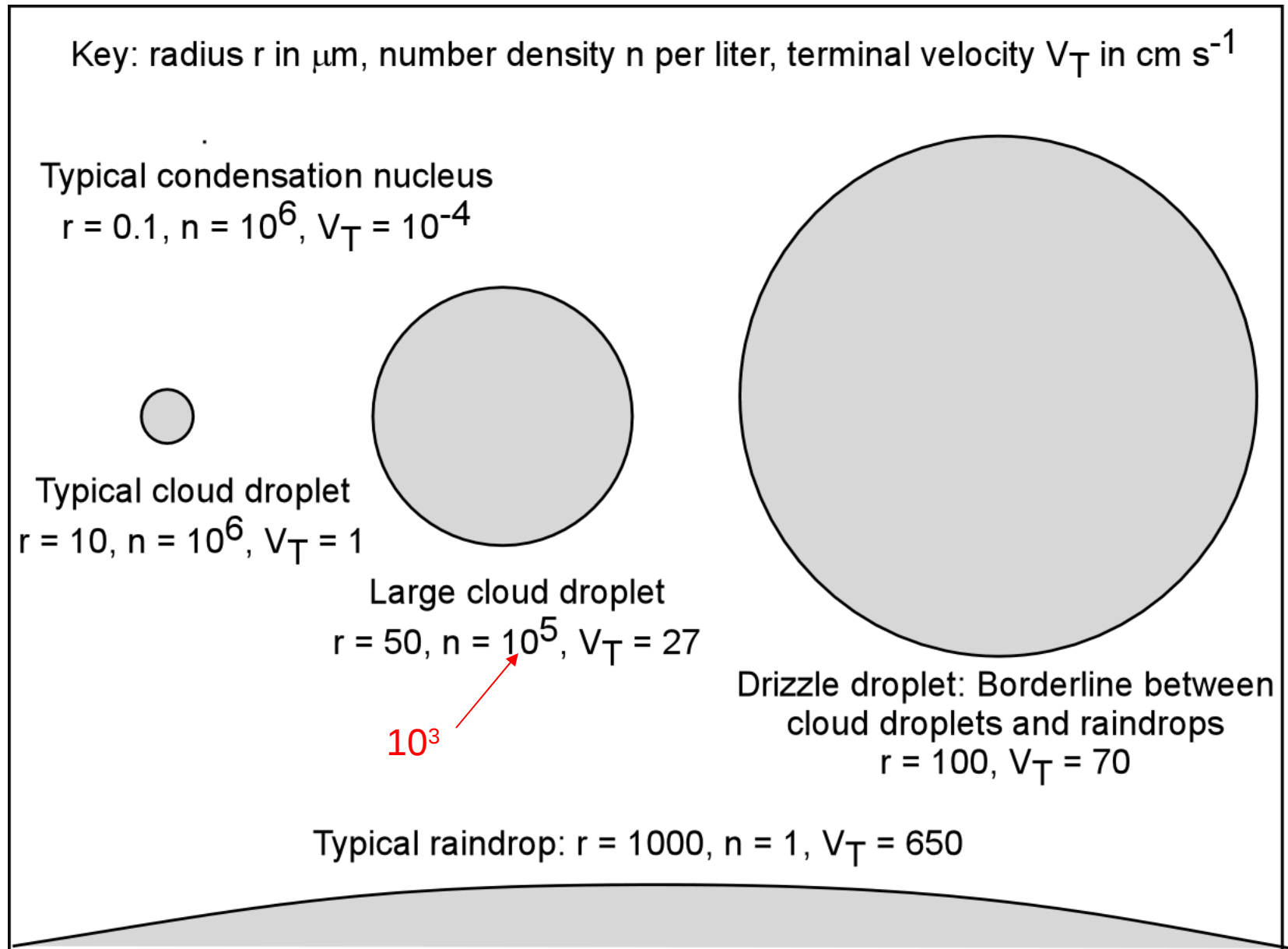## Surface Thermodynamics and Nucleation of Water Droplets and Ice Crystals

Nucleation: the formation of cloud droplets and ice crystals, involving a change of phase (vapor to liquid, vapor to solid, liquid to solid)

Question: What physical processes promote the *nucleation* within warm and cold clouds?

Warm cloud – T > 0 °C everywhere; or, a cloud that is entirely liquid.

Cold cloud – T < 0 °C somewhere; or, a cloud that has some ice.

The nucleation of a water droplet and growth to a raindrop spans four orders of magnitude in size, ranging from O(0.1 μm) for a CCN to O(1 mm) for a rain drop

Key: radius r in μm, number density n per liter, terminal velocity V_T in cm s^{-1}

Typical condensation nucleus
r = 0.1, n = 10^6, V_T = 10^{-4}

Typical cloud droplet
r = 10, n = 10^6, V_T = 1

Large cloud droplet
r = 50, n = 10^5, V_T = 27

10^3

Drizzle droplet: Borderline between cloud droplets and raindrops
r = 100, V_T = 70

Typical raindrop: r = 1000, n = 1, V_T = 650

9.1.1 Review of Gibbs and Helmholtz free energy

From Chap. 4:

Gibbs free energy

$$g = u - Ts + p\alpha$$

$$dg = du - Tds - sdT + pd\alpha + \alpha dp = -sdT + \alpha dp.$$

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

We have considered thermodynamics in terms of bulk properties (e.g., p, T, ρ, r_v, etc).

When cloud droplets or ice crystals form, a surface (discontinuity) is formed.

Thus, we need to examine surface effects.

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 **surface tension** is defined as the work per unit area (A) done in extending the surface of the liquid (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.

The Gibbs function takes on two additional terms related to the additional energy and work alluded to in the previous section:

<div style="text-align:center">chemical   surface
potential   tension</div>

$$dg = -sdT + \alpha dp + \Sigma \mu_i dn_i + (\partial g/\partial A)dA, \qquad (9.1)$$

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,

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

The second term on the RHS, $\sum e_i$, is related to the work of expansion *plus* other forms of work, such as last two terms on the RHS of Eq. (9.1).

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

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

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

$$\sigma = 76.10 - 0.155T \quad \text{(units: erg cm}^{-2}\text{; T in }°\text{C; recall that 1 J = 10}^7\text{ erg).}$$

A plot of this function is provided on an attached figure (Fig. 5-1 from Pruppacher and Klett, 1978). 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 my 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), $(NH_4)_2SO_4$ (ammonium sulfate), NH_4Cl (ammonium chloride), and NH_4NO_3 (ammonium nitrate) solutions.

9.1.4 Hydrostatic pressure difference over a curved surface

Relation between work of expansion and surface tension. For an increase in radius 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

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

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

$$p_i - p_o = 2\sigma/r. \qquad\qquad (9.2)$$

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 and is therefore greater for small drops.

9.2. Nucleation of cloud droplets (vapor → water)

Homogeneous vs. Heterogeneous nucleation will be considered.

9.2.1 Homogeneous nucleation

Definition: 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 (or persist).

Assume that this droplet has a volume V and surface area A.

The change in Gibbs free energy (due to condensation) of the system is

$$nV(\mu_v - \mu_l).$$

The work involved is $A\sigma$, where σ is the surface tension, or the work required to create a unit area of the vapor-liquid interface. This is _not_ an equilibrium transformation, that is

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

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

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

where Δg is the net increase of energy of the system due to the formation of the drop.

We previously determined (Section 5.2) that the change in chemical potential ($\mu_v - \mu_l$) can be expressed in terms of bulk thermodynamic quantities (T and relative humidity, or saturation ratio $S = e/e_s$) as

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

We can then write

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

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

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

$$\Delta g = 4\pi r^2 \sigma - (4/3)\pi r^3 nkT\ln(e/e_s). \qquad\qquad (9.3)$$

Surface
effects

Change in
chemical potential

The equilibrium vapor pressure over a curved surface exceeds that over a flat surface at the same temperature. Eq. (9.3) is a illustrates this.

The first term is related to surface effects and the second depends on 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*:

$$R = 2\sigma / nkT\ln(e/e_s). \qquad\qquad (9.4)$$

Fig 4.10 (W&H) below plots Eq. (1) for positive and negative values of $\ln(e/e_s)$ 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	2.2×10^{-1}	1.42×10^{-7}
1.01	1.1×10^{-1}	3.56×10^{-8}
1.02	5.4×10^{-2}	8.99×10^{-9}
1.05	2.2×10^{-2}	1.48×10^{-9}
1.10	1.1×10^{-2}	3.88×10^{-10}
1.50	2.6×10^{-3}	2.14×10^{-11}
2.00	1.6×10^{-3}	7.34×10^{-12}
3.00	9.8×10^{-4}	2.92×10^{-12}
4.00	7.8×10^{-4}	1.86×10^{-12}

_____

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

$$\frac{n_R}{n_v} = \varepsilon \xi \pi \frac{-\Delta g_{\mu}\alpha\xi}{kT} \qquad (9.5)$$

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 (nR) of pure water at T=20 ℃.

e/e_s	n_R (per liter)
1.005	0
1.01	0
1.10	0
1.50	0
2.00	5×10^{-61}
3.00	2×10^{-13}
4.00	4×10^{-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 nR 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:

$$\nu = \frac{e}{(2\pi m k T)^{1/2}} \tag{9.6}$$

where e is in mb. For water this reduces to

$$\nu = 6.21 \times 10^{21} e T^{-1/2}.$$

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
$$\nu_c = 7.81 \times 10^{22} R^2 e T^{-1/2}.$$
The initial nucleation rate, J, is given by
$$J = n_R \nu_c.$$
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 → ice)

Deposition process vs. condensation considered previously.

The latent heating is greater.

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 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 → ice)

This represents the second path that is theoretically available for homogeneous ice nucleation.

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 not well known, 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}.)

Based on laboratory experiments, *in situ* cloud measurements, and remote sensing of clouds (e.g., lidar with depolarization capability) virtually all (cloud) water is 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

The only homogeneous nucleation process active in clouds is through the water-ice phase (freezing by -40 °C) transition.

Measurements of S ($=e/e_s$) within clouds rarely exceed 1.01 (near cloud base). In rare instances, S may approach 1.1 in real clouds with strong updrafts. (We will consider a conservation equation for S in Chap. 7.)

This implies that homogeneous nucleation does not occur, since the required S for embryonic droplets at radius 0.1 µm exceeds 1.01.

Review of homogenous nucleation

$$\Delta g = 4\pi r^2 \sigma - (4/3)\pi r^3 nkT\ln(e/e_s).$$

$$R = 2\sigma / nkT\ln(e/e_s).$$
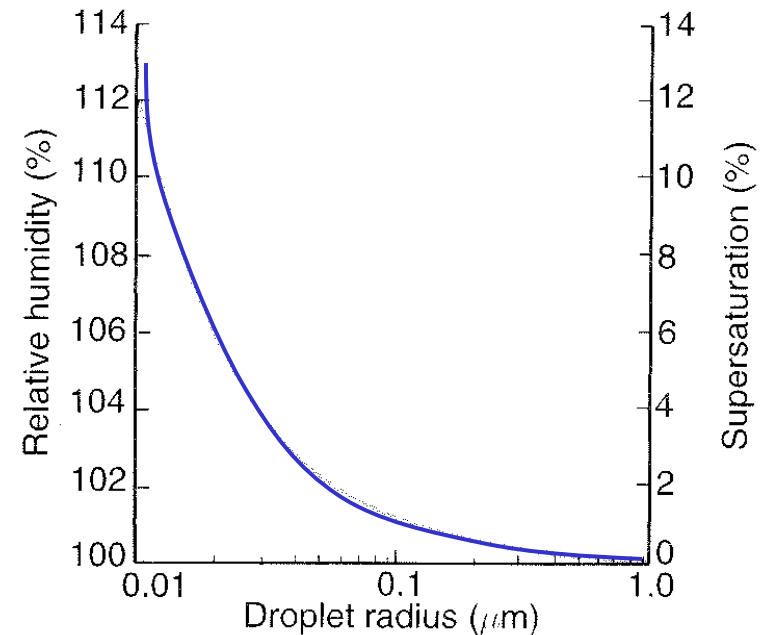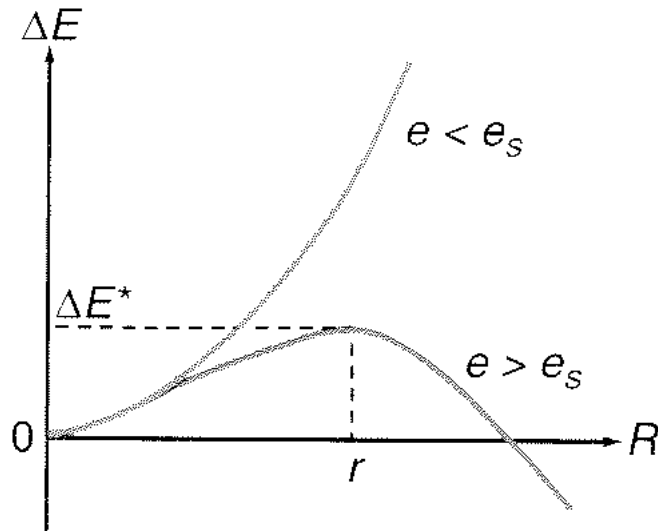
Increase ΔE (Δg) in the energy of a system due to the formation of a water droplet of radius R from water vapor with a pressure e; e_s is the saturation vapor pressure with respect to a plane surface of water at the temperature of the system. From Wallace and Hobbs.

The relative humidity and supersaturation (both with respect to a plane surface of water) at which pure water droplets are in (unstable) equilibrium at 5 °C. From Wallace and Hobbs.

9.3   Heterogeneous nucleation of water droplets

The formation (homogeneous nucleation) of droplets in a pristine atmosphere is a difficult process requiring appreciable supersaturation.

For heterogeneous nucleation, the presence of foreign particles relaxes the constraints that are present for homogeneous 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 ~10^{-4} to ~100 µm, 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 µm),
large particles (0.2 < r < 2.0 µm),
giant particles (r > 2.0 µm).

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 μm)

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)

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 µm, 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

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

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.
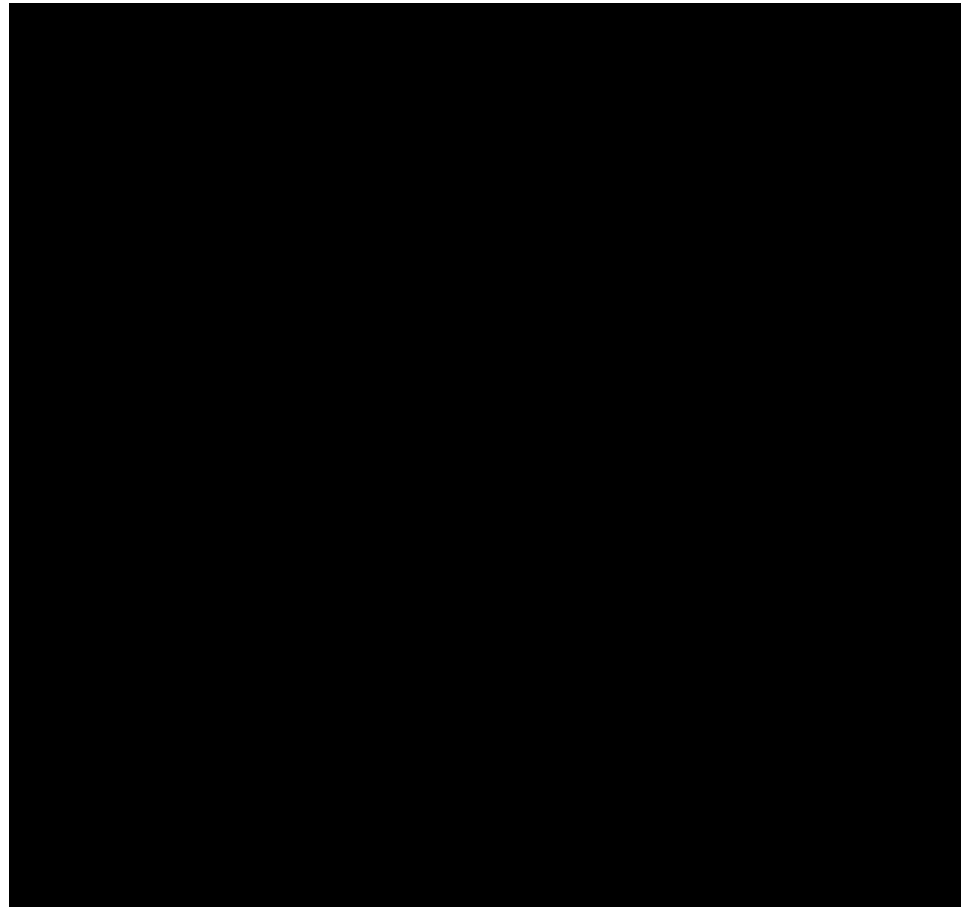
es

Marine air mass

Arctic air

Cloud condensation nucleus spectra in the boundary layer from measurements near the Azores in a polluted continental air mass (top line), in Florida in a marine air mass (middle line), and in clean air in the Arctic (bottom line). From Wallace and Hobbs.

CCN concentrations 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 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 [$(NH_4)_2SO_4$ - prominent over continents] are particularly efficient CCN.

(Consider NaCl here. Fig. from Wallace and Hobbs)

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

$$e'/e_s = f = n_0 / (n_0 + n') \approx 1 - n'/n_0 \qquad (n' << n_0) \qquad (9.8)$$

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 (~2). Then

$n = iN_0M/m_s$ (N_0 - Avogadro's no., M - mass of solute, m_s - molec. weight of solute)

$n_0 = N_0m/m_v$ (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

$$e'/e_s = 1 - [3im_vM/4\pi\rho_Lm_s] \, r^{-3} = 1 - br^{-3}. \qquad\qquad (9.9)$$

From the Kelvin Eq. (9.4) we can write

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

For the dissolved substance the above eq. is modified to

$$S = e'/e_s = \exp[(2Mr)/(R_vT\rho_Lr)].$$

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

For small a/r, $e^{a/r} = 1 + a/r + (a/r)^2/2 + \ldots \approx 1 + a/r$, we can write

$$e_s'(r)/e_s(\infty) = (1-br^{-3})(1+ar^{-1})$$

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

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

$$e_s'(r)/e_s(\infty) \approx 1 \quad + ar^{-1} \quad - br^{-3} \qquad\qquad (9.10)$$
$$\text{curvature term} \quad \text{solute term}$$

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:

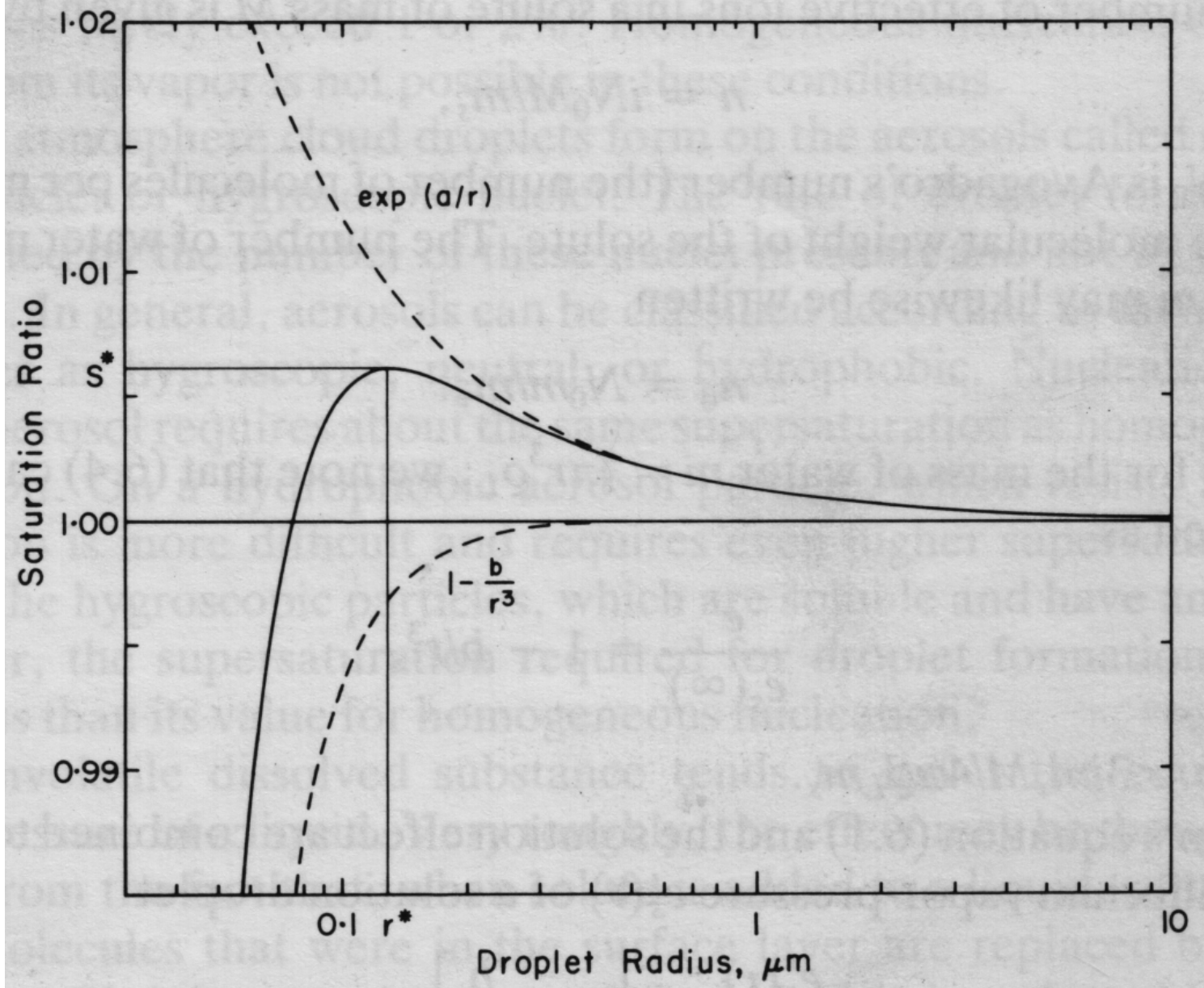$$r^* = [3b/a]1/2; \qquad S^* = 1+[4a^3/27b]^{1/2}. \qquad\qquad (9.11), (9.12)$$

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).

Variations of the relative humidity and supersaturation adjacent to droplets of (1) pure water (blue) and adjacent to solution droplets containing the following fixed masses of salt: (2) 10^{-19}. kg of NaCI, (3) 10^{-18} kg of NaCI, (4) 10^{-17} kg of NaCI, (5) 10^{-19} kg of $(NH_4)_2SO_4$, and (6) 10^{-18} kg of $(NH_4)_2SO_4$. Note the discontinuity in the ordinate at 100% relative humidity. From Wallace and Hobbs.

Kohler curves 2 and 5 from the figure in the upper left. Curve 2 is for a solution droplet containing 10^{-19} kg of NaCl, and curve 5 is for a solution droplet containing 10^{-19} kg of $(NH_4)_2SO_4$. From Wallace and Hobbs.

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 μm.

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 μm 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.

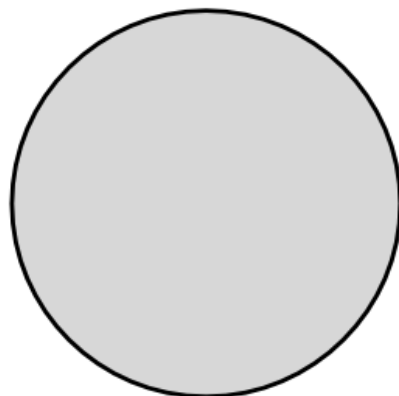Key: radius r in μm, number density n per liter, terminal velocity V_T in cm s^{-1}

Typical condensation nucleus
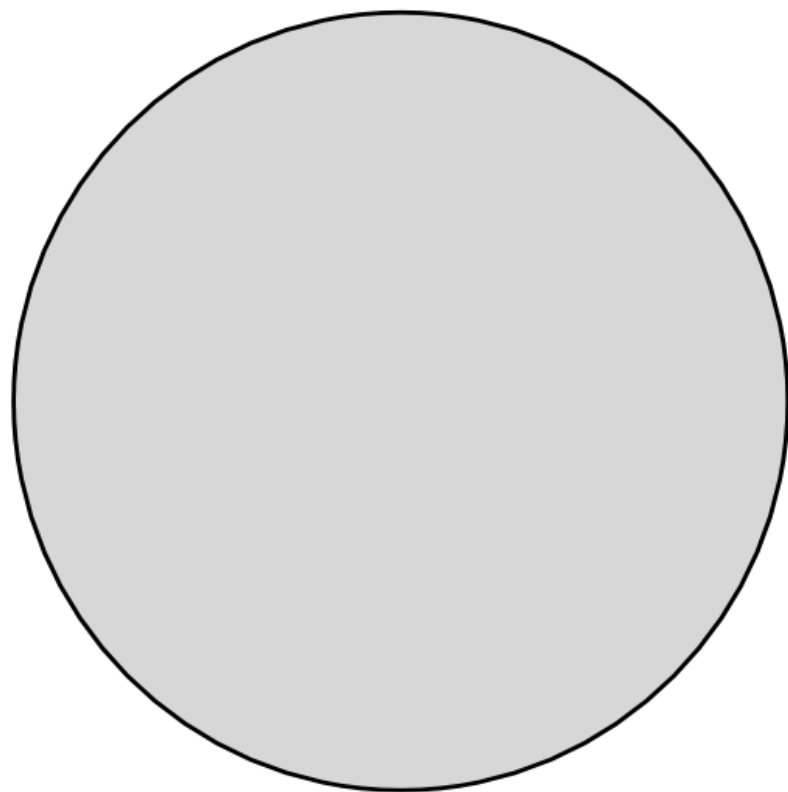$r = 0.1$, $n = 10^6$, $V_T = 10^{-4}$

Typical cloud droplet
$r = 10$, $n = 10^6$, $V_T = 1$

Large cloud droplet
$r = 50$, $n = 10^3$, $V_T = 27$

Drizzle droplet: Borderline between
cloud droplets and raindrops
$r = 100$, $V_T = 70$
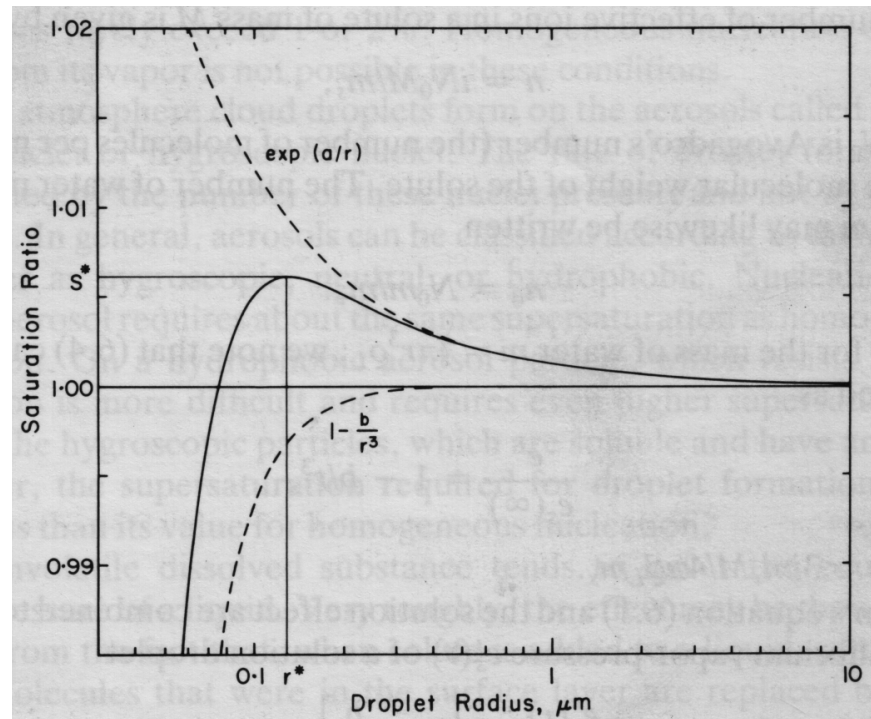
Typical raindrop: $r = 1000$, $n = 1$, $V_T = 650$

Review of heterogenous nucleation of water droplets

$$\Delta g = As \;-\; nVkT\ln\frac{e}{e_s} = 4\pi r^2 s \;-\; \frac{4}{3}\pi r^3 nkT\ln\frac{e}{e_s}$$

$$\frac{\partial(\Delta g)}{\partial r} = 0 \qquad R = \frac{2s\,(T)}{nkT\ln(e/e_s)}$$

$$or \;\; \frac{e}{e_s} = \exp\frac{2s}{nkTR}$$

Either of these equations can be used to define the (unstable) equilibrium value of R or e/e_s.

The presence of dissolved salt reduces the equilibrium vapor pressure to e'/e = f, where e' is the reduced vapor pressure. It can be shown that
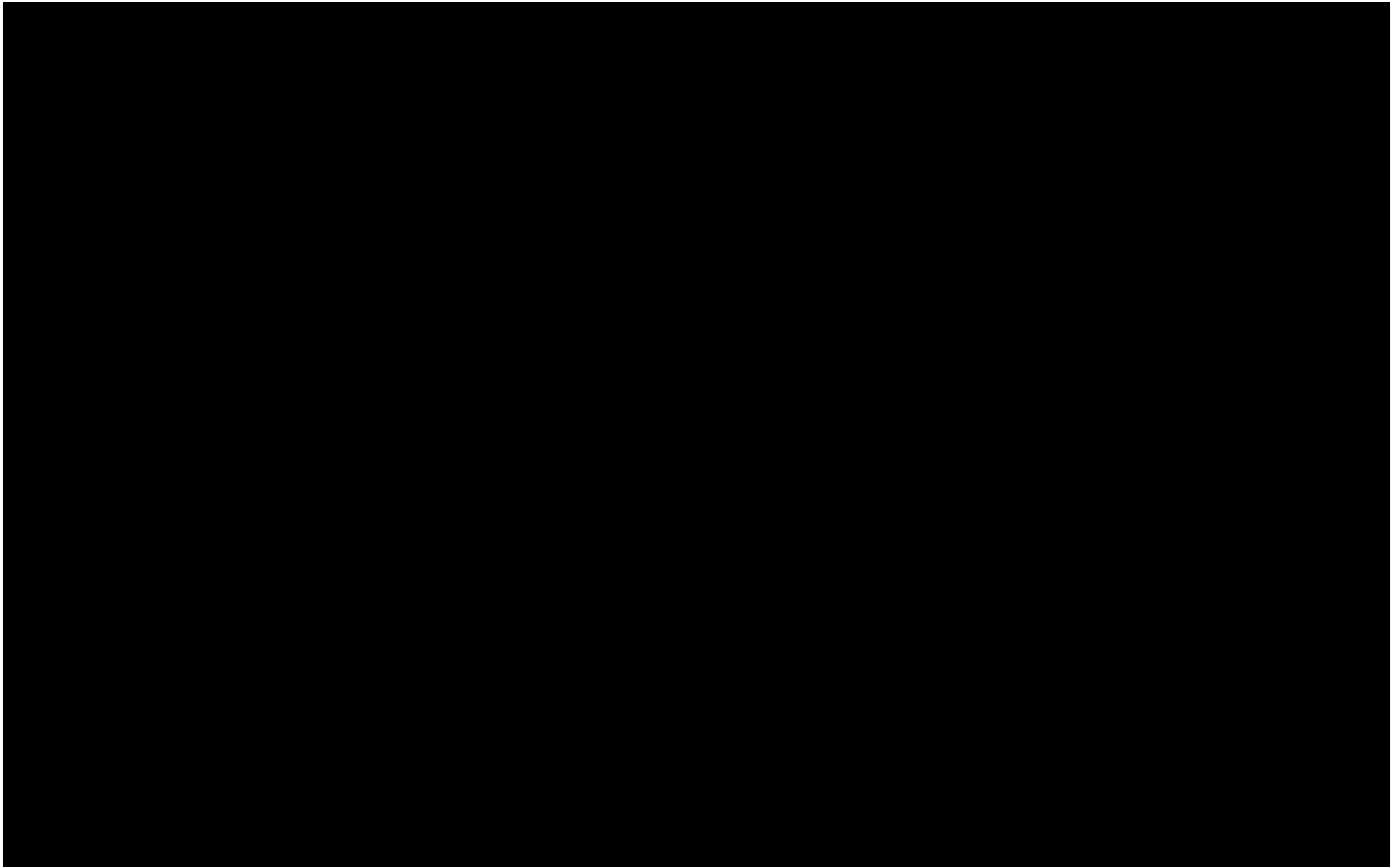
$$\frac{\varepsilon}{\varepsilon^{TM}} = 1 - \frac{3\mu_\sigma M}{4\pi\rho_\Lambda\mu_\sigma}\rho^{-3} = 1 - \beta\rho^{-3}$$

This is multiplied with the Kelvin Eq. to get

$$\frac{e'}{e_s} = \frac{e}{e_s}\frac{e'}{e} = \exp\left[\frac{2s}{nkTR}\right]\left(1 - br^{-3}\right)$$

$$\approx 1 + ar^{-1} - br^{-3}$$

Plots of e'/e$_s$ vs. r are called *Kohler* curves

Assignment

- Problems 6.3 and 6.10 in Rogers and Yau