THERMODYNAMICS OF CHARGE ENHANCED NUCLEATION AND CLOUD DROPLETS FORMATION AND GROWTH:

By

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Abstract

In this study we considered thermodynamics of the atmosphere,under this We have seen moist air humidity variables mean molecular weight of moist air and other quantities and we derived the virtual temperature T_{vrt}.We also considered surface tension and nucleation of cloud droplets. we studied homogeneous and heterogeneous nucleation as well as droplet growth and derived the change in droplet radius r_d.

The result shows that droplet radius grows as the square root of time and how the droplet radius reduces in time through evaporation. In addition to this, we considered thermodynamics of charge enhanced nucleation formation and growth, the source of charge droplet which are,charge separation by the differential motion of drops of different sizes, or the always-present electric current between ionosphere and the Earths surface, which can charge up individual droplets at cloud boundaries. The result shows increasing the charge Q also increases the amount of work done against the electrostatic potential.

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Chapter 1

Introduction

Thermodynamics deals broadly with the conservation and conversion of various forms of energy and the relationships between energy and the changes in properties of matter.The concepts of classical thermodynamics were developed from observations of the macroscopic properties of physical, chemical, and biological systems. In the early part of the 20^{th} century, it became apparent that the empirically-derived laws of thermodynamics are deducible by application of classical and quantum mechanical principles to atoms; this is known as statistical thermodynamics or statistical mechanics. We draw upon classical thermodynamics to describe what happens in a thermodynamic process, while using the molecular view of statistical thermodynamics to increase our understanding of why. Why do we need an understanding of thermodynamics to study the atmosphere and ocean? Some of the reasons include [1]

a) The forces that drive the motions of the atmosphere and ocean are created by differential heating of the Earth's surface and atmosphere by the sun. Because of the Earth's spherical shape and axial tilt, the tropics receive more energy than the poles. Furthermore, the heat capacities of water, land, and air are very different, as are the efficiencies at which they absorb solar radiation. Differential heating spanning a wide range of spatial scales creates thermodynamic imbalances, which in turn create winds and ocean currents as the atmosphere/ocean system attempts to return to thermodynamic equilibrium [1].

b) Changes of phase of water in the atmosphere result in the formation of clouds and precipitation. Associated with the formation of clouds and precipitation are the release of latent heat and modifications to atmospheric radiative transfer. Freezing and melting of seawater in high latitudes influences profoundly the manner in which heat is exchanged between the atmosphere and ocean [1].

c) Accounting for heat exchanges in the atmosphere and ocean is essential in any predictive model of the ocean and/or atmosphere, for any space or time scale that is considered [1].

d) Thermodynamic feed backs in the atmosphere and ocean are critical to understanding climate change. For example, increasing the concentration of carbon dioxide in the atmosphere tends to heat the planet. However, changes in the amount and phase of water in the atmosphere and at the Earth's surface caused by this warming may enhance or mitigate the warming.

A thermodynamic system is a definite quantity of matter which can exchange energy with its surroundings by performing mechanical work or by transferring heat across the boundary. A system may be open or closed, depending on whether or not it exchanges matter with its environment. A system is said to be isolated if it does not exchange any kind of energy with its environment.

A thermodynamic state variable is a quantity that specifies the thermodynamic state of a substance (e.g., temperature). For a closed system, the mass and chemical composition define the system itself; the rest of the properties define its state. For a homogeneous system of constant composition, there are three variables that describe the state of the substance, only two of which are independent. These variables are the pressure p, the volume V, and the temperature T. If any two of the three thermodynamic variables are known, then the value of the third will be fixed, because the variables are related in a definite way. Thus for a homogeneous system we have the following equation of state relating the three variables:

$$F(P, V, T) = 0 \tag{1.0.1}$$

For an ideal gas, we have the familiar equation of state,

$$PV = nRT \tag{1.0.2}$$

where n is the number of moles and R is the universal gas constant. Thermodynamic variables and the functions derived from these variables are called extensive if they depend on mass (e.g., volume, internal energy), and intensive if they do not depend on mass and can be defined for every point of the system (e.g. temperature, density). Intensive variables are particularly advantageous in studying atmospheres and oceans since they make keeping track of the number of moles, mass, etc. unnecessary in these large thermodynamic systems [2].

The Earth's atmosphere consists of a mixture of gases, water in the vapor, liquid and solid states, and other solid particles that are very small in size. The Earth's atmosphere up to about 110 km (the homosphere) is well mixed by turbulent air motions, and the composition and concentration of the passive constituent gases (i.e., those that do not undergo phase changes or extensive chemical reactions) is fairly constant with height. Above the homosphere, the composition of the heterosphere (or exosphere) is subject to diffusive stratification by the molecular weight of the gases and strong chemical and photochemical alterations. The focus here is on the composition of the homosphere. The concentrations of the major gaseous constituents in the homosphere (N_2 and O_2) constitute approximately 99% of the volume and mass of the homosphere [2]. The concentrations of the gases are relatively constant throughout the homosophere, with the exception of water vapor.

There are many other gases present in trace amounts in the homosphere that are importance in atmospheric chemistry and radiative transfer, including ozone, methane, nitrous oxide, sulfur dioxide. Water vapor constitutes 0 to 4% of the atmospheric concentration of gases, the exact amount varying with time and location.

the distribution of water vapor in the atmosphere and how it varies with height and latitude. The maximum concentration near the surface of the Earth indicates that the surface is the principal source of atmospheric water vapor. The general decrease in water vapor concentration above the Earth's surface arises from condensation that occurs in clouds. Water vapor is the most important gas in the atmosphere from a thermodynamic point of view because of its radiative properties as well as its ability to condense under atmospheric conditions. Water is the only substance in the atmosphere that occurs naturally in all three phases.

In addition to the gaseous constituents and condensed water particles, the atmospheric composition includes aerosol particles that are suspended in the air. Atmospheric aerosol particles are composed of dust, sea-salt particles, soil particles, volcanic debris, pollen, by-products of combustion, and other small particles that arise from chemical reactions with in the atmosphere.

In chapter two,We will consider,thermodynamics of the atmosphere, basically moist air, humidity variables, mean molecular weight of moist air and other quantities and we derived the virtual temperature T_{vrt}. In chapter three,we would to investigate the change in droplet radius r_d. the result shows,the droplet radius grows as the square root of time and how the droplet radius reduces in time through evaporation. finally, We will see charge enhanced nucleation, formation and growth, source of the charge and factors affecting the size of the droplet.

Chapter 2

Thermodynamics of the atmosphere

2.1 Moist air

Our atmosphere is basically a two-component system. One component is dry air and the other is water existing in vapor and possibly one of the condensed phases (liquid water or ice) [1,2]. According to Daltons law, in a mixture of ideal gases each gas can be assumed to behave as if the other gases were absent. As such, in a mixture of dry air, water vapor, and a condensed phase, the water system(water vapor plus condensed phase) can be treated as being independent of the dry air. In this case, (for the one-component heterogeneous system water) are valid for the two-component heterogeneous system dry air plus water [2].

We will call the system consisting of dry air and water vapor moist air and it can be unsaturated or saturated with water vapor. Since liquid water is absent, moist air is a two-component system with one phase present. we need three state variables to specify the systems state. Usually these variables are taken to be pressure, temperature, and a new variable (to be defined soon) called mixing ratio. If the condensed phase is present and in equilibrium with the vapor phase, then two variables are needed (typically temperature and pressure). For clarity i will use the subscripts d, w, v to indicate dry air, liquid water, and water vapor, respectively. The only exception will be for the vapor pressure, which we will denote simply as P_v. Variables with no subscripts will correspond to a mixture of dry air and water vapor [2].

2.2 Humidity variables

In a sample of moist air, dry air and water vapor have the same temperature T and occupy the same volume V . Thus, for water vapor

$$P_vV = m_vR_vT \tag{2.2.1}$$

or

$$P_v = \rho_vR_vT \tag{2.2.2}$$

. where P_v is the vapor pressure, ρ_v is the density of water vapor, and R_v is the specific gas constant for water vapor. Similarly for dry air, we have

$$P_d = \rho_dR_dT \tag{2.2.3}$$

. where P_d is the dry air pressure, ρ_d is the density of dry air, and R_d is the specific gas constant for dry air. Since he molecular weight of water.

$$M_V = 18.01mol^{-1} \tag{2.2.4}$$

the value of R_v is equal to

$$\frac{R*}{M_v} = 461.5Jkg^{-1}k^{-1} \tag{2.2.5}$$

Since $R^* = R_dM_d$ it follows that,

$$R_dM_d = R_vM_v \tag{2.2.6}$$

$$\epsilon = \frac{M_v}{M_d} = \frac{R_d}{R_v} = 0.622 \tag{2.2.7}$$

We define the specific humidity, q, and mixing ratio, ω, as

$$q = \frac{\rho_v}{\rho} = \frac{m_v}{m} \tag{2.2.8}$$

$$\epsilon = \frac{R_d}{R_v} \tag{2.2.9}$$

and

$$\omega = \frac{\rho_v}{\rho_d} = \frac{m_v}{m_d} \tag{2.2.10}$$

where $m = m_d + m_v$ is the total mass of the mixture (ρ_v is also called the absolute humidity) [1]. Using Eq (2.2.2) and (2.2.3) and $p_d = p - p_v$ it follows that

$$\omega = \epsilon \frac{p_v}{p - p_v} \tag{2.2.11}$$

At saturation the saturation mixing ratio is

$$\omega_s = \epsilon \frac{p_{vs}}{p - p_{vs}} \tag{2.2.12}$$

where p_{vs} is either the equilibrium (saturation) vapor pressure with respect to liquid water p_{vsw} or with respect to ice p_{vsi}. In general $p_{vs}, p_v << p$ which reduces the above two equations to $\omega \approx \epsilon \frac{p_v}{p}$,$\omega_s \approx \frac{p_{vs}}{p}$ since $\frac{1}{q} = (m_d + m_v)/m_v + 1$ it follows that

$$\frac{1}{q} = \frac{1}{\omega} + 1 \tag{2.2.13}$$

$$\omega = \frac{q}{1-q} \tag{2.2.14}$$

,

$$q = \frac{\omega}{1+q} \tag{2.2.15}$$

In the atmosphere both ω and q are very small ($\omega, q << 1$) .[2,3] For this reason we can always assume that $\omega \approx q$. The relative humidity, r, is defined as

$$r = \frac{m_v}{m_{vs}} \tag{2.2.16}$$

where m_v is the mass of water vapor in a sample of moist air of volume V and m_{vs} is the mass of water vapor the sample would have had if it were saturated. Because of the ideal gas law we can write r as $r = \frac{p_v}{p_{vs}}$ it follows that approximately

$$r = \frac{\omega}{\omega_s} \tag{2.2.17}$$

[2,3].

2.3 Mean molecular weight of moist air and other quantities

we have that the mean molecular weight of moist air is

$$\bar{M} = \frac{m_d + m_v}{\frac{m_d}{M_d} + \frac{m_v}{M_v}} \tag{2.3.1}$$

We can manipulate the above equation by writing it as

$$\frac{1}{\bar{M}} = (\frac{m_d}{M_d} + \frac{m_v}{M_v})(\frac{1}{m_d + m_v}) \tag{2.3.2}$$

or

$$\frac{1}{\bar{M}} = \frac{1}{M_d}[\frac{1}{m_d + m_v}(m_d + \frac{m_v + M_d}{M_v})] \tag{2.3.3}$$

$$or \frac{1}{\bar{M}} = \frac{1}{M_d}\frac{m_d}{m_d + m_v}(1 + \frac{m_v/m_d}{M_v/M_d}) \tag{2.3.4}$$

or

$$\frac{1}{\bar{M}} = \frac{1}{M_d}\frac{1}{1 + \omega}(1 + \frac{\omega}{\epsilon}) \tag{2.3.5}$$

since

$$\frac{1}{\bar{M}} = \frac{1}{M_d}(\frac{1}{1 + \omega} + \frac{q}{\epsilon}) \tag{2.3.6}$$

or

$$\frac{1}{1+\omega} = \frac{q}{\omega} \tag{2.3.7}$$

and

$$\omega = \frac{q}{1-q} \tag{2.3.8}$$

then

$$\frac{1}{\bar{M}} = \frac{1}{M_d}(1 - q + \frac{q}{\epsilon}) \tag{2.3.9}$$

or

$$\frac{1}{\bar{M}} = \frac{1}{M_d}[1 + (\frac{1}{\epsilon} - 1)q] \tag{2.3.10}$$

or

$$\frac{1}{\bar{M}} = \frac{1}{M_d}(1 + 0.61q) \tag{2.3.11}$$

Then for moist air the equation of state is

$$p^a = R_{moist}T = \frac{R^*}{\bar{M}}T = \frac{R^*}{M_d}(1 + 0.61q)T = R_d(1 + 0.61q)T \tag{2.3.12}$$

The above equation defines the virtual temperature,

$$T_{virt} = (1 + 0.61q)T \tag{2.3.13}$$

which can be interpreted as the temperature of dry air having the same values of p and a as the moist air. Otherwise stated, virtual temperature is the temperature that air of a given pressure and volume (or density) would have if the air were completely free of water vapor. Since q in reality is always greater than zero, T_{virt} is always greater than T. The above equation also gives the gas constant of the mixture:

$$R = (1 + 0.61q)Rd \tag{2.3.14}$$

Similarly, we can define the specific heat capacities of moist air. Suppose that a sample of such air receives, at a constant pressure, an amount of heat (δQ) which increases its temperature by (δT) . Some of this amount (δQ_d) is absorbed by the dry air and some (δQ_v) by the water vapor [3].

2.4 Nucleation and diffusional growth

Nucleation is a process where by a stable element of a new phase first appears within the initial or ”parent” phase. Phase transition does not occur under conditions of thermodynamic equilibrium, since a strong energy barrier must be surmounted for a phase to be nucleated if the new phase has higher atomic order than the parent phase [1,2]. The energy barrier arises when a surface must be formed between the two phases. Most of the nucleation processes in the atmosphere and the ocean occur through heterogeneous nucleation [1,2].

The specific nucleation processes of interest here are the nucleation of water drops from water vapor, the nucleation of ice crystals from water drops or from vapor, and the nucleation of ice crystals in sea water to form the initial sea ice cover. Once a phase has been nucleated, it can undergo diffusional growth if environmental conditions are favorable. Diffusion of water vapor to a cloud drop or ice crystal results in growth by condensation and deposition respectively. Diffusional cooling of the initial sea ice cover causes further growth of the sea ice [3,4].

2.4.1 Surface tension

In contrast to gases, which expand to fill the volume of their container, condensed phases can sustain a free boundary, or surface, and occupy a definite volume. The interface between a liquid and its vapor is not a surface in the mathematical sense, but rather a zone that is several molecules thick, over which the concentration of water molecules varies continuously [2,3].

A molecule at the surface of a liquid is free to move along the surface or into the interior of the liquid, in which case its place on the surface is taken by another molecule. However, a molecule can not move freely from the interior of the liquid to the surface. The water molecules that form the free surface of a body of water are subjected to intermolecular attractive forces exerted by the neighboring liquid water molecules just beneath the surface. Therefore, the force field surrounding a molecule at the surface of a liquid is not symmetrical, and the molecule experiences a net force from the other molecules towards the interior of the liquid. If the surface area is increased, for example by changing the shape of the container, water molecules must be moved from the interior to the surface. To move a molecule from the interior to the surface of the liquid, work must be done against the intermolecular forces.

The energy of a molecule at the surface of a liquid is thus higher than the energy in the interior. We can therefore consider the formation of a liquid surface as representing an increase in potential energy. For bulk water, such as the liquid in a drinking glass, the surface tension is a negligible part of the total potential energy, and the surface is fiat rather than curved. The surface potential energy is a significant fraction of the total potential energy for small drops, since they have a large surface to volume ratio and curvature. A sphere has the smallest surface area for a given volume, and hence the smallest surface energy. The spherical shape of cloud drops is a consequence of the minimum-energy principle [3].

We can extend the thermodynamic equations to include surface effects with the introduction of surface tension work, W_{st}. For the work required to extend a liquid surface against its vapor, we can write

$$dW_{st} = \sigma dA \tag{2.4.1}$$

where dA is the change in surface area and σ is the surface tension between two phases. The surface tension is defined as the surface potential energy per unit surface area. The augmented form of the combined first and second laws for a thermodynamic system for which the surface energy is significant can be written in terms of the Gibbs function as

$$dG = \eta dT + VdT + VdP + \sigma dA \tag{2.4.2}$$

.

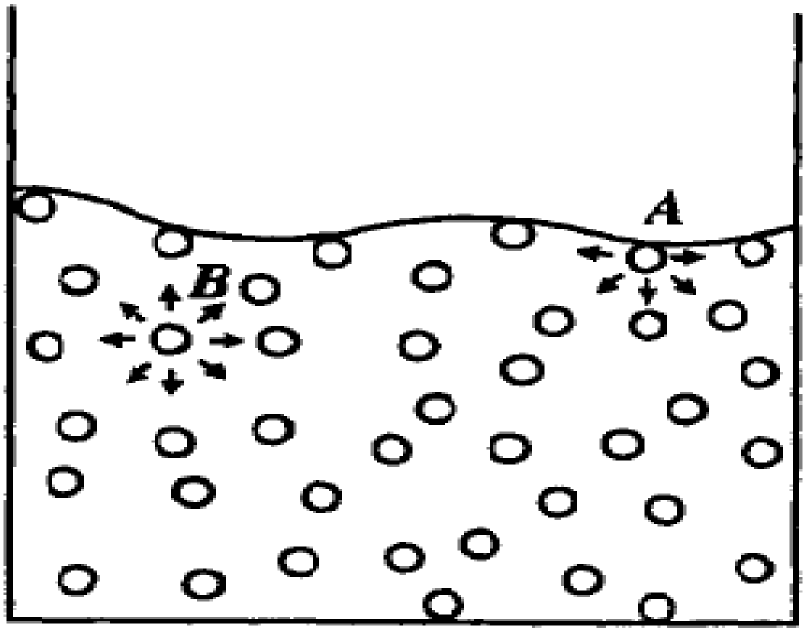

Figure 2.1: Water molecules at the surface of a liquid are subjected to a different attractive force field than those in the interior. A surface molecule, A, experiences a net attractive force towards the interior of the liquid. An interior molecule, B, experiences a symmetric force field exerted by its neighboring molecules and therefore does not freely move to the surface.

2.4.2 Nucleation of cloud drops

A small fraction of collisions between water vapor molecules in the atmosphere are inelastic, leading to the formation of molecular aggregates. The size of an aggregate can be increased by inelastic collisions between molecular aggregates, or by accretion of individual molecules. Most aggregates have a short lifetime, since they disintegrate under continual molecular bombardment. When an aggregate attains a size sufficient for survival, then nucleation of a water drop has occurred [2].

Because of surface tension effects, the escaping tendency of the water molecules in a spherical drop is reduced, and equilibrium vapor pressure over a spherical drop can be substantially greater than values derived for bulk water without significant surface tension effects. The higher value of saturation vapor pressure over a curved surface relative to a bulk flat surface at the same temperature is a consequence of the work that must be performed on the system to increase the drop's surface area. For a drop with surface area $A = 4\pi r^2$ the surface tension work is determined from

$$dW_{st} = \sigma_{lv} 8\pi r dr \tag{2.4.3}$$

where σ_{lv} is the surface tension between the liquid and vapor phases. Since the work of expansion against a difference in pressure must equal the work done in changing the surface drop area,

$$\sigma_{lv} d_A = \Delta p dv \tag{2.4.4}$$

where Δp, is the pressure differential between the external ambient pressure and the internal pressure of the drop. For a spherical drop, we can write.

$$\sigma_{lv} 8\pi r dr = \Delta p 4\pi r^2 dr \tag{2.4.5}$$

$$\Delta p = \frac{2\sigma_{lv}}{r} \tag{2.4.6}$$

. Note that the smaller the drop, the larger the pressure differential. Under standard atmospheric conditions, the internal pressure of a drop with μm radius is $1.5 atm$. The existence of this excess internal pressure in a small drop is a fundamental consequence of the surface tension. The surface tension for the vapor-liquid interface of water,σ_{lv}, is a function of temperature and is given by.

$$\sigma_{lv} = 0.0761 - 1.55 \times 10^4 T \tag{2.4.7}$$

To determine the conditions for nucleation of a water drop, we use Gibbs function

$$dG = -\eta dT + vdp + \sigma_{lv} dA + \mu_l dnl + \mu_v dnv \tag{2.4.8}$$

If we assume that nucleation occurs at constant temperature and pressure, and that $dn_l = -dn_v$, we have

$$dG = \sigma_{lv} 8\pi r d_r + (\mu_l - \mu_v) dn_l \tag{2.4.9}$$

Since dG is an exact differential, we can consider nucleation to occur in two stages first, the bulk condensation of supersaturated water vapor onto a plane surface; and second, the formation of drops from the bulk water. For the first stage, we can write as

$$dG = (\mu_l - \mu_v) d_{nl} \tag{2.4.10}$$

The term $(\mu_l - \mu_v)$ can be evaluated as follows. For an isothermal process involving one mole of water vapor, we can write

$$d\mu_v = dG = R^* T d(\ln p_v) \tag{2.4.11}$$

or

$$\mu_v = \mu_{v^0} + R^* T \ln \frac{p_v}{p_{v0}} \tag{2.4.12}$$

where μ_v^0 is a reference chemical potential that varies only with temperature and p_{v0} is the corresponding reference vapor pressure. At saturation, we can write

$$d\mu_{vs} = dG = R^* T d(\ln p_{vs}) \tag{2.4.13}$$

and,

$$\mu_{vs} = \mu_{v^0} + R^* T \ln \frac{p_{vs}}{p_{v0}} \tag{2.4.14}$$

Since $\mu_l = \mu_{vs}$ when the two phases are in equilibrium over a plane surface, we can therefore write

$$\mu_l - \mu_v = R^* T \ln(\frac{p_{vs}}{p_v}) \tag{2.4.15}$$

The number of moles of water vapor, dn_v,that condense onto spherical drops can be written

$$dn_v = \frac{1}{M_v} dm_v = \frac{\rho l}{M_v} 4\pi r^2 dr \tag{2.4.16}$$

Substitution of (2.7.15) and (2.7.16) into (2.7.13) yields

$$dG = (-R_v T \ln \frac{p_v}{p_{vs}} \rho_l 4\pi r^2 + \sigma_{lv} 8\pi r) dr \tag{2.4.17}$$

Integration of (2.7.17) for the nucleation process gives

$$\Delta G = 4\pi r^2 \sigma_{lv} - \frac{4}{3} \pi r^3_{\rho l} R_v T \ln \varsigma \tag{2.4.18}$$

where $\varsigma = p_{vs}(r) \diagup p_{vs}$ is the saturation ratio and p_{vs} is the saturated vapor pressure over a plane surface [5].

Chapter 3

Thermodynamics of nucleation formation and growth

3.1 Homogeneous nucleation: the kelvin effect

Homogeneous Nucleation refers to nucleation of pure phase of one component. Naively, we would expect vapour to start to condense and thus form cloud droplets if the relative humidity is above 100% [5].However, we have to be careful the saturation vapour pressure is only valid for flat water surfaces.Cloud droplets have strongly curved surfaces and as a consequence the surface tension needs to be incorporated in the free energy budgets [2].The surface tension effect is named after William Thomson, Lord Kelvin, who made many seminal contributions to thermodynamics and physics in general [1].

Any liquid gas interface experiences a surface tension. The surface tries to contract like an elastic membrane.Therefore, increasing the surface area of such an interface requires work energy.The amount of work required dW is proportional to the increment in surface area dA with the proportionality constant called surface tension γ [7]

$$dW = \gamma dA \tag{3.1.1}$$

The unit of surface tension is Jm^{-2} or, equivalently Nm^{-1}. It is the surface tension that makes droplets (and bubbles) spherical. The surface tension tries to minimize the surface area of a drop for the volume of the drop given. The shape that has minimum surface area for a given volume is a sphere [5]. A typical value for the surface tension of a water air interface is $\gamma = 75 \times 10^{-3} Nm^{-1}$. Surface tension reduces with increasing temperature but the reduction is small. The linear approximation is accurate to within one part per thousand in the range of $0^0c < T < 40^0c$ [3]. For many practical purposes we take γ to be constant.

The origin of surface tension is the relatively strong attractive force between molecules in a liquid; it takes energy to separate the molecules of a liquid. It can be seen that molecules at the surface of the liquid have fewer neighbours than molecules in the bulk of the liquid [1]. In order to reside at the surface the molecule must separate from some of its surrounding molecules. This separation costs energy and the total energy involved will be proportional to the number of molecules that reside at the surface, which is again proportional to the surface area of the liquid. This explains that any increase of surface area will correspond to a proportional increase in energy [6].

The molecules in the bulk of the liquid are attracted by more neighbours than molecules at the surface and therefore have a lower potential to gamma energy [1,2]. The total potential energy of the liquid is minimized when the surface area is minimum for a given bulk volume [1]. The increase of potential energy with surface area manifests itself as surface tension. On increasing the temperature of the liquid it becomes easier to sever the link between the liquid molecules because the kinetic energy of the molecules helps to overcome the energy barrier between the bound and separated states. This means that at higher temperatures the excess energy to enable a molecule to reside at the surface becomes lower.

As a result, the surface tension decreases with increasing temperature. Any evaporation from such a surface would decrease the surface area and thus release energy

[3,4]. The internal energy budget for a liquid drop is therefore modified to

$$du_1 = Tds_1 - pdv_1 + \gamma dA \tag{3.1.2}$$

Transforming this to a Gibbs function budget we find

$$dG_1 = -S_1 dT + V_1 dp + \gamma dA \tag{3.1.3}$$

This modified Gibbs function budget forms the basis of a modified Clausius Clapeyron equation. A flat surface is of course also under surface tension, but any evaporation from a flat surface does not change its surface area, so does not contribute to the Gibbs function budget. This is why in the derivation of the ClausiusClapeyron equation in the surface tension did not play a role [2]. For a spherical liquid drop, the area change δA is related to a mass transfer δM from the liquid to the vapour phase (so a positive δM corresponds to a reduction in droplet volume V) as

$$\delta A = \frac{dA}{dv} \tag{3.1.4}$$

$$\delta v = \frac{dA}{dv} v_1 \tag{3.1.5}$$

$$\delta M = \frac{2v_1}{r} \delta M \tag{3.1.6}$$

with v_1 the specific volume of the liquid phase and r the radius of the droplet. Here we take it that for a spherical droplet.

$$v = (\frac{4}{3}) \pi r^3 \tag{3.1.7}$$

and

$$A = 4\pi r^2 \tag{3.1.8}$$

and write

$$\frac{dA}{dv} = (\frac{dA}{dr})/(\frac{dv}{dr}) \tag{3.1.9}$$

Following on from Eq (2.1.3), the change of the Gibbs function δG at fixed temperature and pressure now becomes

$$\delta G = M_1(-s_1\delta T + V_1\delta e) + M_V(-S_V\delta T + v_v\delta e) + (g_v - g_1 - \frac{2\aleph}{r})\delta M \qquad (3.1.10)$$

Because by construction, $\delta G = 0$, $\delta T = 0$,and $\delta e = 0$ we find that, $g_v = g_1 + \frac{2\gamma v_1}{r}$ This equation can be used to calculate the change in the vapour pressure for a given temperature due to surface tension. At a fixed temperature we find,

$$(\frac{\partial g_v}{\partial p})_T\delta p_v = (\frac{\partial g_1}{\partial p})_T\delta p_v + 2\gamma v_1\delta(\frac{1}{r}) \qquad (3.1.11)$$

using $(\frac{\partial g}{\partial p})_T = v$ and assuming $v_1 << v_v$ we find,

$$V_v\delta p_v = 2\gamma v_1\delta(\frac{1}{r}) \qquad (3.1.12)$$

We can next use the ideal gas law to write $V_v = R_v\frac{T}{p_v}$ and arrive at

$$R_vT\frac{\delta p_v}{p_v} = 2\gamma v_1\delta(\frac{1}{r}) \qquad (3.1.13)$$

At fixed temperature T and assuming V_1,γ and $R_V$are not functions of the radius, this can be integrated between the case of a flat surface with radius $r \rightarrow \infty$ and a curved surface of radius r [1]. The vapour pressure e then varies between its flat surface value, $p_{vs}(\infty)$as determined by the ClausiusClapeyron equation, and its curved surface value $p_{vs}(r)$, which we are trying to calculate. The integral becomes

$$R_vT\ln\frac{p_vs(r)}{p_{vs}(\infty)} = \frac{2\gamma v_1}{r} \qquad (3.1.14)$$

This is written in terms of a saturation ratio S_k as

$$S_k = \frac{p_{vs(r)}}{p_{vs}(\infty)} = \exp(\frac{2\gamma v_1}{R_vTr}) \qquad (3.1.15)$$

The curvature effect increases the saturated vapour pressure compared to its flat surface value that is, $S_k > 1$. This effect is called the Thomson effect or the Kelvin effect [4,5]. A physical picture for the Kelvin effect is that for a drop under surface tension it is easier to evaporate water because the associated reduction of droplet radius releases surface energy. The effective energy barrier for evaporation has therefore reduced. The relative humidity and the saturation ratio can be compared. For example, if

$$RH > S_k \tag{3.1.16}$$

where RH- is Relative Humidity [2]. the drop is in a supersaturated environment and vapour will condense on it; the drop will grow. A flat surface has a saturation ratio of 1 and therefore the vapour will condense on it when the relative humidity is above 100%. Curved drops have higher saturation ratios and therefore need a higher relative humidity. (above 100%.) to grow [3,4].

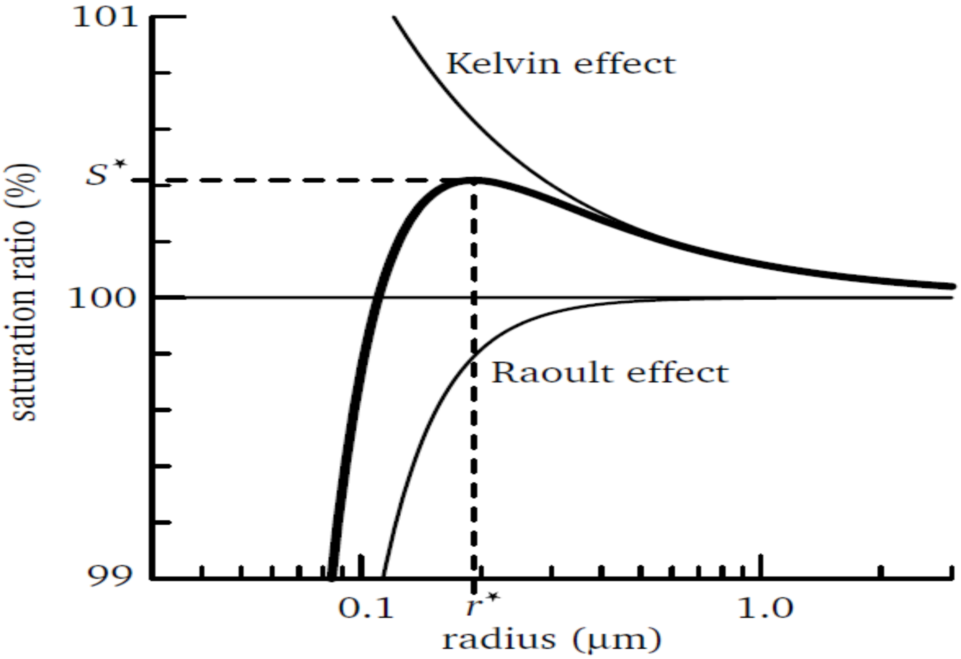

Figure 3.1: Saturation ratio as a function of droplet radius (eKNohler curvef, thick line) for a droplet at 0^0c and with 10^{-16} g of NaCl solute. The KNohler curve is the product of the Kelvin effect and the Raoult effect (thin lines)

The Kelvin effect is small for large droplet radii. It becomes very large for radii r smaller than the Kelvin radius r_k with

$$r_k = \frac{2\gamma v_1}{R_v T} \tag{3.1.17}$$

For water drops at typical atmospheric temperatures, $r_k \approx 1.2nm.$ about 10 times the size of a water molecule. A drop of water of size r_k would therefore contain several thousand water molecules; this is getting close to the regime where equilibrium thermodynamics becomes less applicable and we need to use molecular dynamics calculations. However, in the atmosphere, typical saturation ratios are only slightly larger than 1 [2,3]. For such saturation ratios we can write

$$S_k \approx 1 + \frac{2\gamma v_1}{R_v T r} \tag{3.1.18}$$

This can be rearranged to

$$\frac{r}{r_k} = \frac{1}{s_k - 1} \tag{3.1.19}$$

So for a droplet with a radius 100 times larger than the Kelvin radius, the Kelvin effect corresponds to a supersaturation of 1 % ($S_k = 1.01$). At such a droplet radius ($\approx 0.12\mu m$) the drop contains enough molecules to be accurately described by macroscopic physics We can rewrite the right-hand side of Equation(2.12)

$$(\frac{\partial g_1}{\partial p})_T \delta p_v + 2\gamma v \gamma_1 \delta(\frac{1}{r}) = (\frac{\partial g_1}{\partial p})_T \delta(p_v + 2\frac{\gamma}{r}) \tag{3.1.20}$$

So the surface tension term in Equation(2.1.1) can be incorporated in the Gibbs function for the drop as

$$g_1(p_v, T) + \frac{2\gamma v_1}{r} = g_1(p_v^{'}, T) \tag{3.1.21}$$

with

$$p_v^{'} = p_v + \frac{2\gamma}{r} \tag{3.1.22}$$

In other words, the surface tension increases the pressure inside the drop by $\frac{2\gamma}{r}$, something that should come as no surprise.So according to Equation(2.1.1) the specific Gibbs functions for the two phases have to be the same as long as the pressure inside the drop is augmented by the capillary pressure

$$P_\gamma = \frac{2\gamma}{r} \tag{3.1.23}$$

compared to the external vapour pressure.

With the interpretation of pressure as a volumetric energy density,the Kelvin effect can be interpreted as a Boltzmann factor corresponding to the excess energy per droplet molecule due to the surface tension

$$\exp(\frac{2\gamma v_1}{R_v T_r}) = \exp(\frac{-\Delta E}{K_B T}) \tag{3.1.24}$$

with the excess energy per molecule written in terms of capillary pressure,

$$\Delta E = -P\gamma \frac{v}{N} \tag{3.1.25}$$

and with N the number of molecules in the drop and V its volume [3]. So the capillary pressure provides a reduced energy barrier between the liquid and the vapour. This interpretation in terms of the Boltzmann factor emphasizes the statistical nature of the vapour liquid equilibrium at a fixed temperature. So can water molecules clump together to form water droplets when the relative humidity is large enough? Such a process is called homogeneous nucleation [1].

Initial clusters of water molecules may form by chance but their radius is quite a bit smaller than 1 nm. This means that the Kelvin effect is important and in practice would correspond to saturation ratios $s_k = 4$ or larger [2]. For growth to occur we would need a relative humidity in excess of 400% or so, see Equation(2.1.7). This never happens in the atmosphere. Homogeneous nucleation cannot be the source of cloud droplets in the atmosphere. Somehow, we need to counteract the Kelvin effect [2,3].

3.2 Heterogeneous nucleation with neutral condensation center

3.2.1 Heterogeneous nucleation:the Raoult effect

Heterogeneous Nucleation refers to nucleation that occurs in the presence of a foreign substance which can reduce the energy barrier to nucleation [5]. The atmosphere contains particles that can serve as condensation nuclei for drops. Many of these particles can partially dissolve in the water they attract [4]. It turns out that the dissolved nucleus in the water reduces the saturation vapour pressure enough to counteract the Kelvin effect.

Suppose the water drop contains number concentrations c_i of solute i; that is c_i of the molecules in the droplet are made up of the solute i. Raoults law now states that the saturated vapour pressure is the sum of the individual saturated vapour pressures of the constituents in the liquid weighted with their number concentrations.

A derivation of Raoults law requires introduction of so-called chemical potentials, the generalized forces that correspond to changes in composition of a substance [4]. An informal justification is as follows. Suppose c is the number concentration of all solute molecules. Then $1 - c$ is the number concentration of water molecules. That means that according to Raoults law the saturated vapour pressure $p_{vs}(c)$ for a water with solute concentration c is

$$p_{vs}(c) = (1 - c)p_{vs}(0) \tag{3.2.1}$$

with $p_{vs}(0)$ the saturated vapour pressure for pure water (with the Kelvin effect included for spherical droplets). From a microscopic point of view this equation makes sense [1]. According to the equipartition theorem, the kinetic energy will be equally distributed amongst all the molecules, because they are at the same temperature. This means that at some temperature the water molecules have the same chance of escaping the solution [3].

It is assumed that the solute does not change the energy barrier for escaping the solution; this is, implicitly, one of the assumptions in deriving Raoults law: the assumption of an ideal solution. However, the number of water molecules per unit number of molecules has reduced by a factor $1-c$, thus reducing the evaporation rate, and therefore the saturation vapour pressure of the water by the same factor. We can rewrite Eq.(2.2.1)in a more explicit form. Write the total number of molecules Nt as

$$Nt = N_l + Ns \tag{3.2.2}$$

with N_l the number of molecules of liquid water, the solvent, and Ns the number of solute molecules.We then find that

$$1 - c = \frac{N_t - N_S}{N_t} = \frac{N_l}{N_l + N_s} = \frac{1}{1 + \frac{N_s}{N_l}} \tag{3.2.3}$$

the fraction $\frac{N_s}{N_l}$ can be expressed as

$$\frac{N_s}{N_l} = \frac{\imath M_s}{\rho_l v} \frac{\mu_l}{\mu_s} \tag{3.2.4}$$

with M_s the total mass of the solute in the drop, V the volume of the drop, being nearly equal to the volume of all the water molecules, and μ_l and μ_s the molar weights of the water and solute molecules, respectively. The factor $\imath$ is the Vant Hoff factor, which takes into account the dissociation of the solute molecules. For example, in solution common salt NaCl will dissociate into two ions, Na^+ and Cl^-. The Van t Hoff factor i is typically equal to 2 for many of the relevant solutes. This expression can be substituted in Eq (2.2.1) to find for the saturation ratio due to the Raoult effect where we have now written $v = (\frac{4}{3})\pi r^3$ for spherical drops of radius r [1].

3.2.2 KOhler theory

Combining the Kelvin and Raoult effects, we get an expression for the ratio of the saturated vapour pressure over a flat surface of pure water to the saturated vapour pressure of a solution in a spherical droplet of radius r at temperature T [4]. This saturation ratio is:

$$S = s_k s_R = \frac{\exp(\frac{a}{rT})}{1 + (\frac{b}{r^3})} \tag{3.2.5}$$

A plot of S as a function of radius is called a Kohler curve. Figure(3.1) shows an example of a Kohler curve highlighting the Kelvin and Raoult effects. The Kohler curve defines at what relative humidity the droplet would be in equilibrium with the environment [3,4]. The maximum of the Kohler curve plays an important role for droplet growth.

The radius at the maximum is called the activation radius, denoted $r^\star$, and the value of the supersaturation at the activation radius is called the activation saturation ratio or critical saturation ratio, denoted $s^\star$ [5]. The values of $r^\star$ and $s^\star$ follow from setting $\frac{d_s}{d_r} = 0$ in the Kohler equation. An exact calculation requires finding the root of a cubic polynomial. However, from the above graph it can be seen that both the Kelvin and Raoult effects are typically quite small around the activation radius (of order one percent).

This suggests that we can use a Taylor expansion for both effects and find an approximate result [5]. To do this, define a non-dimensional radius x as

$$r = x\sqrt{\frac{bT}{a}} \tag{3.2.6}$$

and a non-dimensional parameter ϵ as

$$\epsilon = \sqrt{\frac{(\frac{a}{T})^3}{b}} \tag{3.2.7}$$

We can write the Kohler curve equation, Eq.(2.3.2),as

$$S(x) = \frac{\exp(\frac{\epsilon}{x})}{1 + \frac{\epsilon}{x^3}} \tag{3.2.8}$$

For typical atmospheric values of the parameters a, b, and T it can be verified that ϵ is quite small. Now assuming that x is not much bigger or much smaller than 1 to be verified in hindsight we can use a Taylor expansion for S in small ϵ ,

$$S(x) = 1 + \frac{\epsilon}{x} - \frac{\epsilon}{x^3} + \varphi(\epsilon)^2 \tag{3.2.9}$$

Setting this to zero gives the non-dimensional activation radius $x^\star$,

$$X^\star = \sqrt{3} + \varphi(\epsilon) \tag{3.2.10}$$

which is indeed not much larger than 1, validating the Taylor expansion The corresponding critical saturation ratio is

$$S^\star = 1 + \frac{2\epsilon}{3\sqrt{3}} \tag{3.2.11}$$

A full solution of $\frac{d_s}{d_x} = 0$ without approximation leads to

$$X^\star = 2\cos[\frac{1}{3}\cos^{-1}(\frac{-\epsilon}{2})] \tag{3.2.12}$$

The difference between this exact expression for $x^\star$ and the approximated expression is small; it can be shown that $x^\star = \sqrt{3} - \frac{\epsilon}{6} + \varphi(\epsilon^2)$

So the non-dimensional parameter $\epsilon$is a measure of the critical supersaturation. Substituting the definitions of x and ϵ , we find the activation radius $r^\star$

$$r^\star = \sqrt{\frac{3bT}{a}} \tag{3.2.13}$$

and the critical saturation ratio $s^\star$

$$s^\star = 1 + \sqrt{\frac{4(\frac{a}{T})^3}{27b}} \tag{3.2.14}$$

The critical supersaturation, defined as $s^\star - 1$, decreases when b increases, which is to say when the amount of solute increases in the droplet. At the same time the activation radius $r^\star$ increases.

Figure (2.2) shows various Kohler curves for different amounts of solute, illustrating the dependencies of $r^\star$ and $S^\star$ on the solute amount. Note that the activation radius is always very small. For any drops larger than about $1\mu m$ both the Kelvin

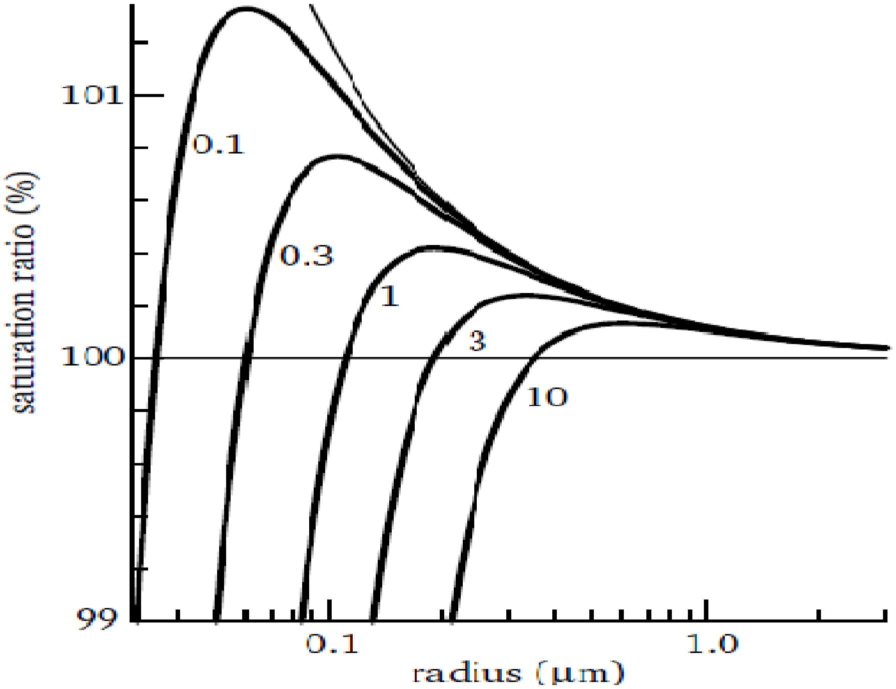

Figure 3.2: Kohler curves for different amounts of NaCl solute $(in10^{-16}g)$. In the limit of vanishing solute amount, the Kohler curve approaches that of the Kelvin effect (thin line)

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and Raoult effects can be ignored. The Kohler curve contains a lot of information about initial cloud droplet growth.

Consider Figure(2.3), where the Kohler curve and the level of the critical saturation ratio divides the figure into three different areas, labelled A, H, and N [1,2]. Now suppose the nucleus has attracted some water and forms a small droplet of a particular radius r. Further suppose this droplet is moved into air of a particular relative humidity RH. This initial droplet then finds itself at the point (r, RH) in the figure and will be in one of the labelled areas [1].

Suppose the initial droplet was some where in area H. In this area the droplet is in an environment with a higher saturation ratio than the equilibrium saturation

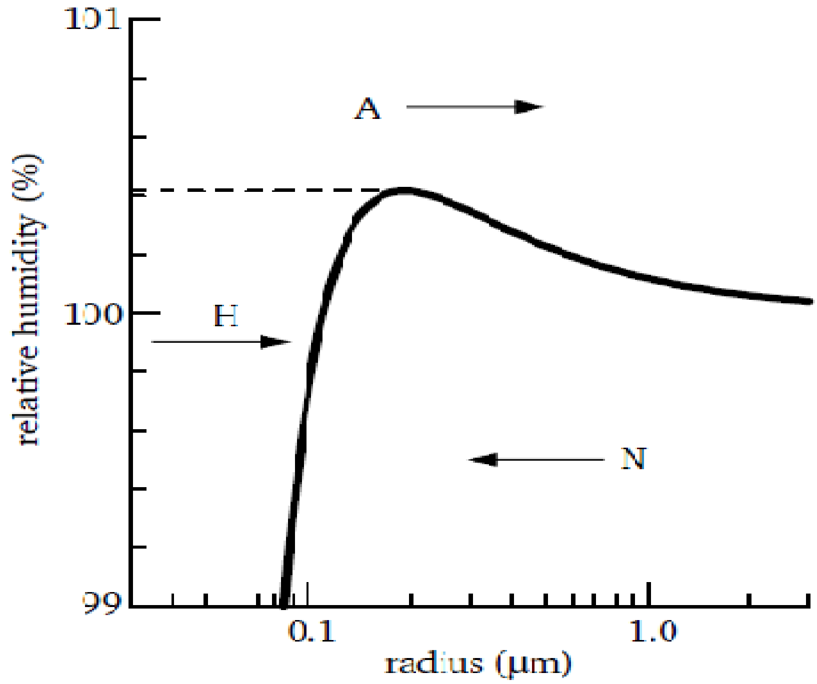

Figure 3.3: Three distinct regions, A, H, and N, in the (r, RH) space, as defined by the Kohler curve

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ratio for the droplet, as given by the Kohler curve. This means that the droplet is in a supersaturated environment and water vapour will start to condense onto the drop [2]. The drop will grow the point (r, RH) in the figure will move to the right, as indicated by the arrow. This growth will continue until the point hits the Kohler curve, where $RH = S$ here the droplet is in equilibrium with its environment and will remain steady [1,2]. Such droplets are called haze.

Suppose the initial droplet was some where in area N. In this area the droplet is in an environment with lower relative humidity than the equilibrium saturation ratio for the droplet. The droplet will therefore start to evaporate and reduce in radius. The point (r, RH) for the droplet will move to the left in the figure until it hits the Kohler curve, where the drop is again in equilibrium, $RH = S$. The droplet has again become haze. To find initial droplets in area N requires the existence of relatively large drops in sub saturated air, which is possible when turbulence is present or when raindrops fall in sub saturated air. Haze droplets on the boundary between areas H and N given by the Kohler curve below the activation radius are stable. if for some reason a haze droplet were to move away from the boundary the tendency would be for the droplet to be pushed back to the boundary. Haze is a stable state for droplets. For larger condensation nuclei the steady radius of haze droplets can be up to several hundreds of nano metres, and therefore become visible [4,5].

Suppose the initial droplet was some where in area A. When considering cloud droplet growth from initial condensation nuclei we start at very small radii. So typically droplets in area A have to be in an environment with a relative humidity higher than the critical saturation ratio $s^{\star}$. The droplet is in a supersaturated environment and will start to grow. But now the growing droplet cannot hit the Kohler curve at any point. it will continue to grow indefinitely and will eventually become a cloud drop. Droplets in region A are said to be activated. For droplets to become activated and grow into cloud drops the environmental supersaturation has to be larger than the critical supersaturation [1]. Typical critical super saturations are less than a couple of percent.

This is the reason why in the atmosphere the relative humidity will never exceed 100% by very much. With any temporary increase in relative humidity, haze droplets would activate and form clouds [1]. These growing cloud droplets would reduce the vapour content of the air until a relative humidity of 100% was achieved and droplets could no longer use up water vapour [4].

3.2.3 Droplet growth

If a cloud droplet is activated it is out of equilibrium. the environment is supersaturated with respect to the droplet and the droplet will grow by condensation of vapour onto the droplet. However, this process is limited by the speed with which the condensed vapour is replenished by new vapour from the environment[5]. If there is no such replenishment, the immediate vicinity of the drop will run out of vapour and will become sub saturated. Consequently, the drop would stop growing˙The process that replenishes the vapour is a diffusive flux of water vapour [1]. To a good approximation, this diffusive flux is proportional to the gradient in water vapour density (Ficks law). So the vapour flux F_v is

$$F_V = -D\nabla\rho_v \tag{3.2.15}$$

where ρ_v is the mass density of the vapour and the constant of proportionality D is called the diffusion coefficient. This sets up a gradient in vapour density between the immediate vicinity of The direction of the flux is opposite to the gradient of the vapour density. mass flows from high densities to low densities.

If a drop is activated, vapour molecules will condense on the drop thus reducing the vapour density in the immediate vicinity of the drop and the far field. This will lead to a diffusive flux of water vapour towards the drop. The value of the diffusion coefficient varies with the species being diffused (approximately with the square root of the mass) and it increases with temperature [2]. For diffusion of water vapour at 5^0C we have

$$D = 22 \times 10^{-6}m^2s^{-1} \tag{3.2.16}$$

with an increase of about $0.15 \times 10^{-6}m^2s^{-1}$ per 1^0c temperature increase. The origin of the vapour flux is the random motion of the vapour molecules [1]. If there is a density gradient there will be fewer molecules moving from the low density to the high density region than the other way around simply because the low density region has fewer molecules to move to the high density region than the other way around. This discrepancy results in a net motion of molecules from the high density area to the low density area [5]. It is also clear that the discrepancy is proportional to the difference in molecule densities between the high and the low density regions.

Assuming the situation is spherically symmetric, all variables will be functions of the radial coordinate r and of time t. We now make the assumption that away from the drop the density field is constant in time (but not necessarily constant in space) [1,3].

The vapour flux F_v is according to Fick's law

$$\hat{F_v} = -\frac{Dd\rho_v \hat{r}}{dr} \tag{3.2.17}$$

with $\hat{r}$ the unit vector in the radial direction. The total mass flux Fm into a shell of radius r then is

$$F_m = -4\pi r^2 F_v = 4\pi D r^2 \frac{d\rho_v}{dr} \tag{3.2.18}$$

Note the sign here: if the vapour density increases away from the drop there will be a positive mass flux towards the drop. F_m is the total vapour mass entering any spherical shell, so it is also the total vapour mass entering the droplet. So the mass growth $\frac{dM_d}{dt}$ of the droplet is

$$\frac{dM_d}{dt} = F_m \tag{3.2.19}$$

The drop grows by condensing the vapour onto its surface. This condensation releases latent heat, which will heat up the drop. In a steady state situation this heat will be conducted away by a total heat flux F_q equal to

$$F_q = -L\frac{dM_d}{dt} = -LF_m \tag{3.2.20}$$

with L the latent heat of condensation and F_q the total inward heat flux through a spherical shell. Note that as the drop grows (F_m positive) the heat flux is directed outward (F_q negative). According to Fouriers law, the heat flux is proportional to the gradient of the temperature. Therefore total inward heat flux is, analogous to Eq.(2.5.4),

$$F_q = 4\pi k r^2 \frac{dT}{dr} \tag{3.2.21}$$

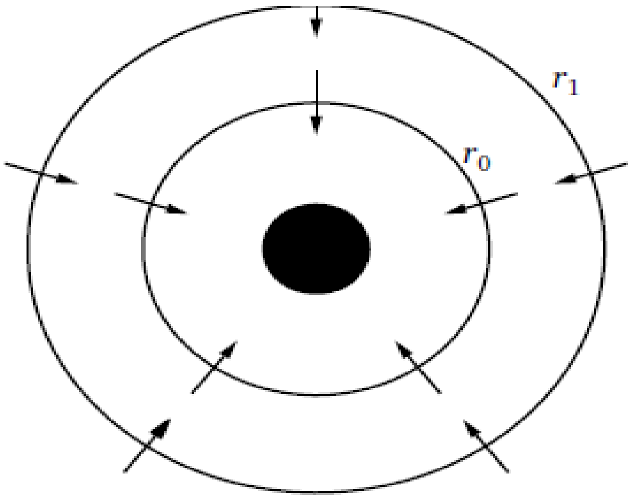

Figure 3.4: Flux of vapour through spherical shells towards a drop. In a steady state the flux through all spherical shells has to be equal.

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with K the heat conduction coefficient. The thermal conductivity of air increases with increasing temperature. A typical value of K at 10^0c is $k = 25 \times 10^{-3} W m^{-1} k^{-1}$ [3] Between -5^0c and 25^0c, K varies only by about 4 percent. In a steady state, the total mass flux into a spherical shell is independent of the radius of the shell. Consider the volume between an outer shell of radius r_1 and an inner one of radius r_0, see Figure 2.5. For a steady state the total vapour mass flux into this volume needs to be the same as the total flux out of this volume. Because this is true for any pair of radii, we have $F_m = constant$ [3]. We can combine this constraint with Ficks law to find a simple expression for the mass flux. [5] First, rewrite Eq.(2.5.4) as

$$\frac{F_m}{r^2} = 4\pi D \frac{d\rho_v}{dr} \tag{3.2.22}$$

Integrating this expression between the droplet radius $r = r_d$ and the far field $r = \infty$ we find

$$\frac{F_m}{rd} = 4\pi D(\rho_v - \rho_v, d) \tag{3.2.23}$$

where we have written ρ_v for the vapour density in the far field (that is, the vapour density of the air not too close to the drop) and ρ_v, d the vapour density at the drop surface. The analogous argument holds for a steady heat flux: the total energy between radii r_0 and r_1 needs to remain constant, so the heat entering the volume must be the same as the heat exiting the volume. This can only be true if F_q is not a function of the radius. This then leads to

$$\frac{Fq}{rd} = 4\pi k(T - T_d) \tag{3.2.24}$$

with T the air temperature in the far field and T_d the temperature at the drop surface [1]. Substituting these expressions in the steady state condition of Eq.2.5.6 we find

$$T - T_d = \frac{-LD}{k}(\rho_v - \rho_v, d) \tag{3.2.25}$$

The temperature difference and the vapour density difference are proportional. For large heat conductivity K, the temperature difference will be small; the latent heat can be efficiently transported away from the drop [4]. For small heat conductivity, the latent heat will accumulate on the drop and larger temperature gradients are required to transport the heat away [1]. The precise meaning of large or small will become clear later on. To calculate the droplet growth we need to know the difference between the vapour density at the drop surface and the vapour density of the air. We assume that vapour near the drop is saturated [4]. Using the ideal gas law we thus have

$$\rho_v, d = \rho_{vs}(T_d) = \frac{p_{vs}(T_d)}{R_v T_d} \tag{3.2.26}$$

We have suppressed the radius dependence of the saturated vapour pressure so this argument is only accurate for drops substantially larger than the activation radius. It is fairly straightforward to include this radius dependence but this would just make the equations more convoluted without providing any further insight. Let us for the moment assume the drop temperature T_d is the same as the air temperature T [2].We then have

$$\rho_v, d = \rho_{vs}(T) = \frac{p_{vs}(T)}{R_v T} \qquad (3.2.27)$$

Using the relative humidity, the vapour density in the far field can be written in terms of the saturated vapour density,

$$\rho_v = RH_{\rho vs}(T) \qquad (3.2.28)$$

With these expressions the total mass flux Fm becomes,

$$F_m = 4\pi D r_d \rho_{vs}(RH - 1) \qquad (3.2.29)$$

where ρ_{vs} is evaluated at temperature T. In other words, the droplet growth is due to supersaturation. If the relative humidity is larger than 100% (positive supersaturation) the drop will grow; if it is smaller than 100% the drop will shrink. So for relative humidities below 100% the above equation can be used to calculate how quickly a droplet evaporates.

Note also that the growing droplets extract water vapour from the air and thus reduce its relative humidity; droplet growth by condensation is a self-limiting process. In the above derivation we took $T_d = T$. As the droplet is heated up by condensation this assumption is not valid. However, assuming that T_d and T are not too far apart we can linearize the saturated vapour pressure in Eq (2.4.15) around temperature T [2].

Now we have an expression for the mass-flux, we can calculate the change in droplet radius r_d. We have

$$F_m = \frac{dM}{dt} = \rho_l \frac{d_v}{dt} = 4\pi \rho_l r_d^2 \frac{d_{rd}}{dt} \qquad (3.2.30)$$

with ρ_l the density of the liquid and V the droplet volume, $v = (\frac{4}{3})\pi r_d^3$. Substituting the expression for the mass flux, we find

$$rd\frac{d_{rd}}{dt} = D\frac{\rho_r}{\rho_l}(RH - 1) \tag{3.2.31}$$

The right-hand side of Eq.(2.4.17) is a constant at given temperature and relative humidity, so we can integrate the equation

$$r_d\frac{d_{rd}}{d_t} = D\frac{\rho r}{\rho l}(RH - 1) \tag{3.2.32}$$

integrating both sides;

$$\int r_d dr_d = \int D\frac{\rho r}{\rho L}(RH - 1)d_t \tag{3.2.33}$$

$$\frac{r_d^2}{2} = D\frac{\rho r}{\rho l}(RH - 1) \tag{3.2.34}$$

$$r_d^2 = 2\alpha t \tag{3.2.35}$$

,where $\alpha = D\frac{\rho r}{\rho l}(RH - 1)$

$$r_d = \sqrt{r_d^2(0) + 2\alpha t} \tag{3.2.36}$$

we have,

$$r_a^2(t) - r_b^2(t) = r_a^2(0) - r_b^2(0) \tag{3.2.37}$$

with r_a and r_b the radii of two different droplets growing in the same background. This is equivalent to

$$r_a(t) - r_b(t) = \frac{r_a^2(0) - r_b^2(0)}{r_a(t) + r_b(t)} \tag{3.2.38}$$

The droplet radius grows as the square root of time. When the relative humidity is smaller than 100%, this equation describes how the droplet radius reduces in time

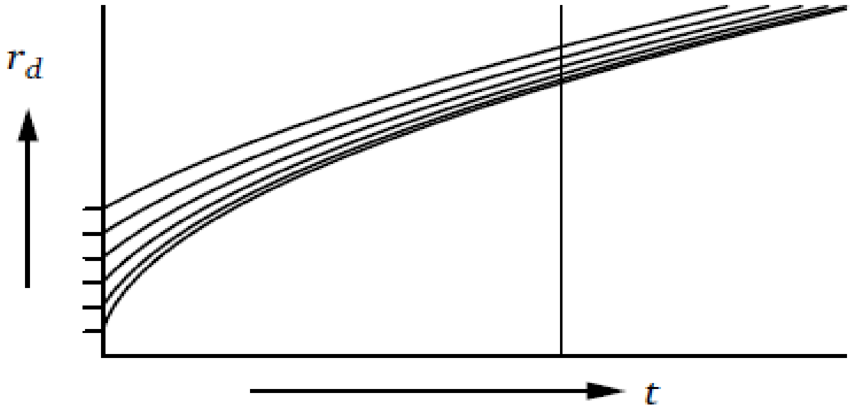

Figure 3.5: Growth of droplet radius through vapour diffusion. The distribution of droplet radii becomes ever narrower.

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through evaporation. Note that with changing droplet radius, the mass flux Fm is not constant in time. Any density fluctuations in the vapour field around the drop will adjust to a steady state through a diffusion process with diffusion coefficient D. The time taken to grow from a small droplet to a typical rain drop of radius about 1mm is several days. Even for growth to modest droplet size of several tens of micro metres we find times of several hours. The typical time scale for rain to form in a convective cloud is very much shorter, perhaps half an hour or less. Diffusive growth cannot be the complete story to go from activation to raindrop. The next stage in droplet growth is described by the process of collision and coalescence. In its simplest form, drops at different radii will fall at different terminal velocities. This then allows the drops to collide and possibly coalesce [2,3].

Chapter 4

Thermodynamics of charge enhanced nucleation formation and growth

Droplets are often charged. There can be many sources of this charge, typically charge separation by the differential motion of drops of different sizes, or the always-present electric current between ionosphere and the Earths surface, which can charge up individual droplets at cloud boundaries [1,2]. A net charge corresponds to an electrostatic energy on the drop which modifies the Gibbs free energy budget and therefore the saturated vapour pressure around the drop [2]. A spherically symmetric charge distribution has an electrostatic potential V_e at radius r of

$$V_e = \frac{Q}{4\pi\epsilon r} \tag{4.0.1}$$

with Q the charge and ϵ the electric permittivity; for all practical purposes we can use ϵ_0 , the permittivity of the vacuum. Increasing the charge by an amount dQ requires work dW against the electrostatic potential of

$$dW = V_e d_Q \tag{4.0.2}$$

So to charge up a sphere from no charge to a total charge Q requires a total electrostatic energy W of

$$W = \frac{Q^2}{8\pi\epsilon r} \tag{4.0.3}$$

For a given charge, a change in the radius of the drop would change the electrostatic energy [2]. That means that on evaporating a mass δm from a charged drop, its electrostatic energy will change. Analogous to the Gibbs function budget is modified to

$$\delta G = (g_v - g_l)\delta M - \frac{Q^2}{8\pi\epsilon r^2}\delta_r \tag{4.0.4}$$

We have ignored any effects of solute or surface tension here in order to isolate the specific effects of the charge and we have omitted the terms proportional to δ_e and δ_T as these are zero by construction. As before,δ_r is related to δ_M The relevant inverse permittivity is

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_{air}} - \frac{1}{\epsilon_{water}} \tag{4.0.5}$$

but the permittivity of water is about 80 times larger than that of air, which in turn is very similar to that of the vacuum,ϵ_0.

$$\delta_r = \frac{\delta_v}{A} = -\frac{v_l}{4\pi r^2}\delta M \tag{4.0.6}$$

with V the volume of the sphere, A its area and v_l the specific volume of the liquid phase (remember that positive δM corresponds to a reduction in droplet volume)[4]. For the variations in the total Gibbs function to vanish, we therefore have

$$g_v(pv, T) = g_l(pv, T) - \frac{Q^2 v_l}{32\pi^2\epsilon r^4} \tag{4.0.7}$$

At infinite radius the charge effect vanishes and the vapour pressure is the same as the flat surface value from the ClausiusClapeyron equation [3]. The result is a new charge-induced saturation ratio S_Q,

$$S_R = \frac{p_{vs}(Q)}{p_{vs}(0)} = \exp(\frac{-Q^2 v_l}{32\pi^2\epsilon R_v T r^4}) \tag{4.0.8}$$

where have returned to the usual notation of p_{vs} for saturated vapour pressure and with $p_{vs}(0)$ the saturated vapour pressure for an uncharged drop. We see that the charge of the drop decreases the vapour pressure around the drop by an exponential factor, $s_R < 1$. This effect is called the Rayleigh effect. The physical picture is that on a charged drop it is more difficult to evaporate water because the associated reduction of droplet radius requires extra electrostatic energy. Analogous to Eq. (2.1.14), the electrostatic term can be absorbed in the pressure dependency of the Gibbs function,

$$g_l(e,T) - \frac{Q^2 v_l}{32\pi^2 \epsilon r^4} = g_l(e',T) \tag{4.0.9}$$

with,

$$e' = e - \frac{Q^2}{32\pi^2 \epsilon r^4} \tag{4.0.10}$$

In other words, the effective pressure inside the drop is decreased by the charge [4]. This decrease of pressure inside a drop should, again, come as no surprise: the repulsive electrostatic charges try to expand the drop. The pressure drop due to the charge is p_Q, with

$$p_Q = \frac{Q^2}{32\pi^2 \epsilon r^4} \tag{4.0.11}$$

The charge effect can be interpreted as a Boltzmann factor,

$$\exp(-\frac{Q^2 v_l}{32\pi^2 \epsilon R_v T r^4}) = \exp(\frac{-\Delta E}{K_B T}) \tag{4.0.12}$$

with the excess energy per molecule written in terms of the pressure drop p_Q due to the charge.

$$\Delta E = \frac{p_Q V}{N} \tag{4.0.13}$$

with N the number of molecules in the drop and V its volume. The charge helps to form droplets by counteracting the Kelvin effect. It is of interest to see when the two effects exactly compensate. Using Eqs.(2.18) and (2.48) we find compensation when $S_k S_R = 1$ or equivalently when

$$P_\gamma = P_Q \tag{4.0.14}$$

For a given charge Q this compensation will occur at a critical radius r_R, the so-called Rayleigh radius, with

$$r_R^3 = \frac{Q^2}{64\pi^2 \epsilon r} \tag{4.0.15}$$

Rayleigh showed that for droplets with a radius smaller than r_R the repulsive electrostatic force becomes so strong that the droplets disintegrate explosively; thermodynamically this can be interpreted as the destabilizing charge pressure overcoming the stabilizing capillary pressure. With the definition of the Rayleigh radius r_R and the Kelvin radius r_K we can rewrite the combined Rayleigh and Kelvin effect to the saturation ratio S as

$$S = S_K S_R = \exp(\frac{r_k}{r}(1 - \frac{r^3 R}{r^3})) \tag{4.0.16}$$

From this equation it becomes clear that the charge effect is only important when the droplet radius is close to the Rayleigh radius. Only for droplets smaller than the Rayleigh radius, the charge effect dominates the Kelvin effect and saturation can occur at relative humidities below 100%. So what is a typical value for the Rayleigh radius? For a unit charge e (an electron has charge -e), we can put in standard values for a water droplet [2]. to find $r_R \approx 0.4nm$. Very tiny indeed; in fact this is so small that quantum effects become important.

For droplets with such high saturation ratios to grow we need relative humidities in excess of RH=400%; this does not occur in nature. We are forced to conclude that in the atmosphere single charge ions cannot serve as condensation nuclei. This is of importance in the present discussion on influence of cosmic rays on climate. Cosmic rays generally produce single charge ions in the atmosphere and it has been argued

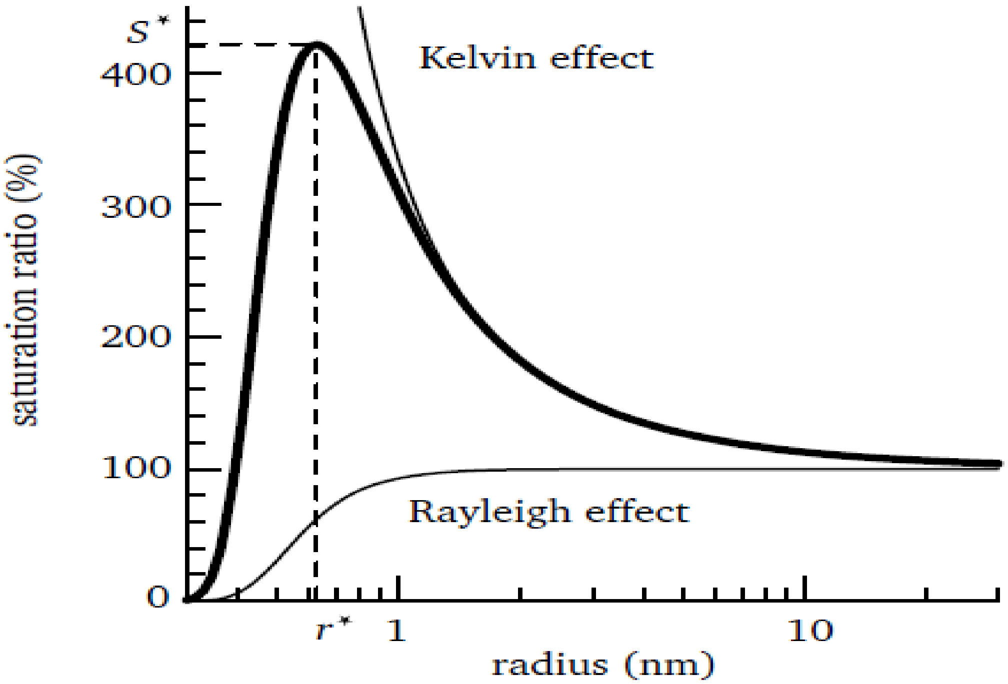

Figure 4.1: Saturation ratio as a function of charged droplet radius for a clean droplet at ^0c with one unit charge.

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that these may form cloud condensation nuclei. It is clear from the argument above that this is impossible. In order for cosmic rays to influence cloud formation other processes such as ion clustering or charge accumulation have to occur. Super saturations of 400% are fairly easy to achieve in the laboratory. By expanding a vessel which has water and its vapour in it we can achieve very high super saturations: on adiabatic expansion the pressure as well as the temperature will drop [2,3]. By the ClausiusClapeyron equation the saturation vapour pressure will also drop and it is found to drop more than the pressure itself. This means that vapour that was originally saturated will become supersaturated. This supersaturation in the laboratory is the basis of the Wilson cloud chamber. Wilson used a closed chamber with saturated vapour and by expansion made the vapour supersaturated. Any condensation nuclei would rapidly saturate and grow into drops. Wilson allowed these drops to settle out. This was repeated until no condensation nuclei were present anymore. Wilson then found that there were still cloud traces in his chamber. Further experimentation with X-ray sources made him realize that these traces were due to charged particles in the cloud chamber, the residual traces being due to natural radioactivity and cosmic rays. The cloud chamber is used as a detector in particle physics [1]. Wilson received the Nobel prize for physics in 1927 for his method of making the paths of electrically charged particles visible by condensation of vapour [4,5].

Chapter 5

Conclusion

In this project we studied Thermodynamics of charge enhanced nucleation and cloud droplets formation and growth. To study Thermodynamics of the Atmosphere, we have seen moist air which is a system consisting of dry air and water vapor. In order to study Humidity variables we have taken moist air,dry air and water vapor with the same temperature T and occupy the same volume V. Here we have seen the factors affecting the specific humidity are, the density of water vapor mass of water vapor and mass of the dry air. We studied surface tension, Here we have seen water molecules at the surface of a liquid are subjected to a different attractive force field than those in the interior. We investigated nucleation of cloud drops and have taken molecular aggregates . As the size of an aggregate increased, the inelastic collisions between molecular aggregates also increased. Finally we studied thermodynamics of charge enhanced nucleation formation and growth, here we have seen the main sources of charge droplets. Typically, charge separation by the differential motion of drops of different sizes or the always present electric current between ionosphere and the Earth's surface which can charge up individual droplets at cloud boundaries.

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DECLARATION

I,here by declare that this master of science is my original work and it has not been presented for a degree in any other university and that all source of materials used for the thesis has been duly acknowledged.

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