

## CHAPTER 4

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# BASIC THERMODYNAMICS

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### 4.1 Thermodynamics

It is immediately apparent to even the casual observer that the influence of temperature, heat flow and energy exchange must play a preeminent role in the study of the snow. In the natural environment snow is always relatively close to its melt temperature, thus, generally defining it as a warm material. While the consequence of this is apparent in the seasonal cycles, it also has a profound effect on its structural morphology and rheological properties. It is very thermodynamically active. In this chapter we present some of the fundamentals of thermodynamics to provide a basis for many of the physical concepts addressed throughout the book. The aim of thermodynamics is to construct a relationship between thermal energy and other forms of energy and work. Classical thermodynamics, utilizes continuum principles in that it deals with systems at a scale that is large enough to measure the relevant parameters while, mathematically, application is considered at the differential scale. Thermodynamic systems are defined in terms of thermodynamic parameters such as temperature, pressure, volume and density, along with a physical boundary that separates the system from its surroundings. The surroundings constitute everything outside of the system. When considering the system we are interested in the balance and flow of energy and mass, both within it and across its boundaries. Clearly defining our system is critical to formulating a well-structured analysis. With respect to its boundaries, there are three types of systems: an isolated system in which there is no heat or mass flow into or out-of the system; a closed system whereby there is no mass exchange; and an open system, which allows both heat and mass to cross the boundary.

An isolated system will tend toward equilibrium, at which point, entropy will be a maximum, the gradients of state variables and the flows are eliminated, and its properties do not change. Classical thermodynamics assumes elements at the local differential scale, for sufficiently short times, to be in “local thermodynamic equilibrium”, although, these elements can move from one equilibrium state to another. This classical approach assumes local processes are reversible for the short time periods between changes of state. Heat and mass flows that occur spontaneously are irreversible. This implies that the original state of the system is only recoverable with the input of work or energy from the surroundings. In actuality, all natural processes are irreversible. However, a quasi-equilibrium process is deemed applicable if all of the intermediate steps are sufficiently close to equilibrium, in which case the state variables are usable at each of these short time steps. This construct works well for assessing many thermodynamic processes and is used extensively in our study of snow.

State variables do not depend on the manner in which they achieve the current state. That is, they are path independent during the transition. Temperature, volume, pressure, density, energy, enthalpy and entropy are state variables, whereas heat flow and work are path dependent.

In Chapter 3, we presented the energy equation, also called the first law of thermodynamics, which provides a means to account for the energy balance of a system. However, it places no restriction on the direction of a process. It is the second law of thermodynamics, along with the concept of entropy, which places the necessary limitations on irreversible processes. The restrictions, defined in terms of an inequality, state that the internal entropy production for a system is always non-negative and in an irreversible process it will be positive. The second law requires that: the internal entropy production - is always greater than, or equal to - the entropy input from the surrounding.

Entropy is a state function conceived to address processes related to heat transfer not covered by the first law. This function, specific entropy (entropy per unit volume),  $s$ , is defined in terms of heat input per unit volume,  $\delta q$ , to the system and the temperature,  $T$ , as

$$ds = \left( \frac{\delta q}{T} \right). \quad (4.1)$$

As stated previously, heat flow is path dependent and not a perfect differential. (This is the reason the notation  $\delta$  is often used instead of the standard,  $d$ , for the differential.) However,  $ds$  is a path independent state variable. The term  $\frac{\delta q}{T}$  is the entropy input from the surroundings. In a cyclic process returning to the original state there will be no change in the entropy of the system,

$$\oint ds = 0. \quad (4.2)$$

For a known heat input and temperature history between two states the change in entropy for a reversible process is

$$s_2 - s_1 = \int_1^2 \left( \frac{\delta q}{T} \right)_{rev}. \quad (4.3)$$

However, in an irreversible process between two states, there will be an increase in the system’s entropy. This increase will be greater than the increase due to external heat input alone,

$$[\Delta s > \int_1^2 \left( \frac{\delta q}{T} \right)]_{irrev}. \quad (4.4)$$

In addition to the entropy brought into the system from the outside, there is an internal entropy production,  $\Gamma$ , which is always positive. This internal entropy production is the result of dissipative processes such as internal friction. A consequence of the second law is that the internal entropy production per unit volume,  $\Gamma$ , is always greater than or equal to zero. That is,

$$\Gamma = \Delta s - \int_1^2 \left( \frac{\delta q}{T} \right) \geq 0. \quad (4.5)$$

#### 4.1.1 Thermodynamic potentials

Thermodynamic potentials are composed of conservative forces that represent the capacity of a system to do work. Particular forms provide information about the available energy under specific constraints. These provide the theoretical basis underlying processes that are of interest to us for snow metamorphism and snow mechanics. The underlying state variable for these potential functions is the internal energy, which includes potential energy such as stored elastic strain energy and molecular kinetic (thermal) energy. Enthalpy, Helmholtz free energy and the Gibbs free energy are useful thermodynamic potentials, which are derivable from the internal energy. Systems tend toward a lower potential, with values going to a minimum at equilibrium.

Continuum based thermodynamics assumes an equation of state for local internal energy per unit volume,  $u$ , with the state defined in terms of, possibly, a collection of substate variables,  $v_i$ , plus specific entropy,  $s$ ,  $u = u(s, v_i)$ . Taking the total derivative of the internal energy with respect to these variables we have,  $du = \frac{\partial u}{\partial s} ds + \frac{\partial u}{\partial v_i} dv_i$ , with the thermodynamic temperature,  $T$ , and general thermodynamic tensions,  $\tau_i$ , defined as  $T = \left( \frac{\partial u}{\partial s} \right)_{v_i}$  and  $\tau_i = \left( \frac{\partial u}{\partial v_i} \right)_s$ . The subscript indicates the variable that is held constant. This then provides the equation of state for the change in internal energy per unit volume

$$du = T ds + \tau_i dv_i \quad (4.6)$$

If thermodynamic tensions,  $\tau_i$  are represented by the stress tensor,  $\sigma$  and the substate variables,  $v_i$ , by the strain tensor,  $\epsilon$ , then

$$du = T ds + \sigma : d\epsilon \quad (4.7)$$

<sup>1</sup> Examining Eq. (4.7) we see that internal energy represents the capacity to release heat and to do work, depicting a form of the energy equation. It will be of use to consider the case of hydrostatic loading of an isotropic material. In this instance, the substate is represented by the volumetric strain,  $v$ , and the thermodynamic tension by the pressure,  $p$ . Then the change of internal energy in local thermodynamic equilibrium for this case may be written as ,

$$du = T ds - p dv. \quad (4.8)$$

<sup>1</sup>The  $:$ , sometimes termed the double dot product, defines the tensor scalar product. In Cartesian coordinates  $\sigma : d\epsilon = \sigma_{ij} d\epsilon_{ij}$ , where Einstein notation ( see Ch. 3) is implied.

Note that in this development we assume the sign convention for a normal stress (i.e. the thermodynamic tension) to be positive when pointing outward from the element, as presented in Ch. 3. Therefore pressure, which implies an inward acting stress, takes on a negative sign. It is also apparent in Eq. (4.8) that internal energy will not change for fixed entropy and volume. If we consider the case of a constant volume and utilize Eq. (4.1),  $Tds = \delta q$ , then we can write,

$$\left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial q}{\partial T}\right)_v = c_{vv}, \quad (4.9)$$

where  $c_{vv}$  is defined as the volumetric heat capacity at constant volume. Specific heat,  $c_v = \frac{c_{vv}}{\rho}$ , is explicitly the heat input required to raise the temperature of a unit mass by a unit temperature.

Enthalpy,  $h$ , represents the capacity to do non-mechanical work and release heat. Enthalpy is of particular relevance to energy balance associated with phase change within the snowpack during metamorphism and at the snow-surface/atmosphere interface. It is defined as,

$$h = u + pv. \quad (4.10)$$

Thus the change in enthalpy is,  $dh = du + pdv + vdp$ , whereupon substituting for  $du$  from Eq. (4.8) yields enthalpy as a function of entropy and pressure,  $h(s, p)$ ,

$$dh = Tds + vdp. \quad (4.11)$$

Consideration at constant pressure yields,  $dh = Tds$ , and using  $Tds = \delta q$  (Eq.4.1),

$$dh = dq. \quad (4.12)$$

From this we have

$$\left(\frac{\partial h}{\partial T}\right)_p = \left(\frac{\partial q}{\partial T}\right)_p = c_{vp}, \quad (4.13)$$

and define the specific heat capacity at constant pressure,  $c_p = \frac{c_{vp}}{\rho}$ .

Although enthalpy is not directly measured, the change in enthalpy is a useful quantity to describe the amount of thermal energy released/absorbed due to a phase change, without the system changing temperature or pressure. The energy exchange required for phase change is often represented by the so called specific latent heat of phase change,

$$L = \Delta h \quad (4.14)$$

Consider, for example, the case of ice sublimation. The values for enthalpy change, or the latent heat of sublimation, account for the energy provided from the surroundings to increase the internal energy of the system from the solid to the vapor state. The opposite situation occurs for the phase change from water vapor to ice. The mass of the ice that changes phase, which constitutes the system in this process, does not itself change temperature or pressure; however, there is an exchange with its surroundings.

Next we introduce the Helmholtz free energy per unit volume,  $\psi$ , which in general represents the maximum capacity of a system to do work in a reversible process. It is defined as,

$$\psi = u - Ts. \quad (4.15)$$

The Helmholtz free energy may be employed in deriving thermoelastic constitutive equations by defining it as a function of strain, temperature and temperature gradient. There are

a number of instances where it is useful to model a snow as an elastic material. Examples include, the slab relevant for slab snow avalanches in fracture studies, rapid loading such as a skier and for compacted snow used for oversnow transport. In the Helmholtz free energy, the thermodynamic tensions,  $\tau_i$  are represented by the stress tensor,  $\sigma$  and the substate variables,  $\nu_i$ , by the strain tensor,  $\varepsilon$ . Substitution of Eq. (4.7) yields,

$$d\psi = \sigma : d\varepsilon - s dT, \quad (4.16)$$

with  $\sigma = \left( \frac{\partial \psi}{\partial \varepsilon} \right)_T$  and  $s = - \left( \frac{\partial \psi}{\partial T} \right)_\varepsilon$ .

Gibbs free energy (sometimes referred to as free enthalpy) represents energy available to do non-mechanical work. It plays a major role in our consideration of the phase changes involved in snow metamorphism. It has the form,

$$g = u + pv - Ts \quad (4.17)$$

or

$$g = h - Ts, \quad (4.18)$$

so

$$dg = -s dT + v dp. \quad (4.19)$$

Gibbs is constant if temperature and pressure are constant, as in the case of phase change. From this, the relation applied to phase equilibrium and the Clausius Clapeyron equation may be derived.

## 4.2 The Clausius Clapeyron Equation - at the basis for Snow Science

The Clausius-Clapeyron (CC) equation states that under equilibrium conditions two phases of a substance will have the same free energy. In the case of water, this relates the saturation vapor pressure over an ice or liquid water surface as a function of the temperature.

The small length scale (mm) of the tortuous pore space in snow restricts airflow. We assume water vapor saturation of the still air in the pore with respect to the surrounding ice matrix. Despite these near equilibrium conditions in the pore space, it is very thermodynamically active. Typically, snow has a temperature gradient and therefore the equilibrium vapor pressure varies locally leading to snow metamorphism and heat transport. Therefore, the CC equation is at the basis of describing heat and mass transport in snow. The fact that phase change is present demonstrates that a true equilibrium does not exist, but the assumption of quasi-equilibrium is reasonable for the conditions present in snow, allowing us to carry out useful calculations.

We first present the CC equation as derived from the Gibbs Free Energy of the phase transition, equating the chemical potential in each phase. Consider that for a single species, in our case water, the chemical potential,  $\mu$ , is equivalent to the Gibbs free energy,  $g$ . Since our interest here will be in snow metamorphism, we consider that the chemical potential along the boundary between the ice and vapor will be equal. In fact, this will be true between any two phases of the water. Consequently, any changes in the chemical potential must be the same in both phases. Now, using Eq. (4.19) for each of the vapor and ice phases, we can write  $d\mu_v = -s_v dT + v_v dp$  and  $d\mu_i = -s_i dT + v_i dp$ , where subscripts indicate the vapor and ice phases, respectively, so that,

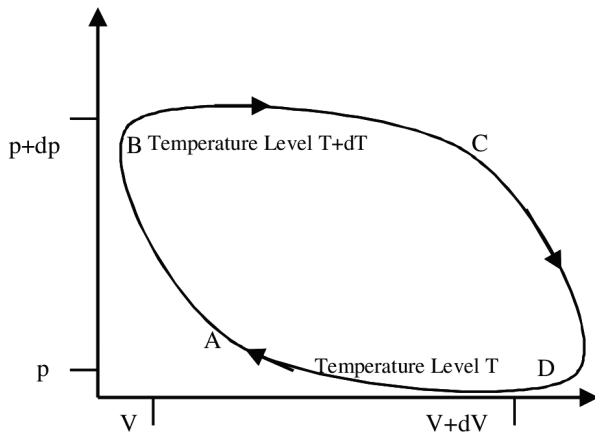
$$-s_v dT + v_v dp = -s_i dT + v_i dp.$$

Additionally, the temperature and pressure will be equal in both phases at the interface. Rearranging,  $dp(v_i - v_v) = (s_i - s_v)dT$  or  $\frac{dp}{dT} = \frac{(s_i - s_v)}{(v_i - v_v)}$ . Now utilizing Eq.(4.11) for a constant pressure during phase change  $dh = Tds$  and by Eq.(4.14) we have  $(s_i - s_v) = L/T$ , so that we arrive at the CC equation,

$$\frac{dp}{dT} = \frac{L}{(v_i - v_v)T} \equiv \frac{L}{\Delta v T} \tag{4.20}$$

It should be made clear that  $\Delta v$  is the volume change before and after phase change for the same material mass.

As an alternative, we next offer an intuitive derivation from first principles by looking at a circular process of phase change with incremental changes/differences in pressure and temperature, Fig. 4.2.



**Figure 4.1** Clausius-Clapeyron: Assuming a circular process in a p-V diagram as an aid for the derivation of the Clausius Clapeyron equation.

We now artificially decompose these incremental pressure, temperature and volume changes, i.e. our circular process into two prescribed adiabatic<sup>2</sup> processes compression ( $A \rightarrow B$ ) and expansion ( $C \rightarrow D$ ) (i.e. perfectly insulated during these processes) and two isothermal<sup>3</sup> processes sublimation ( $B \rightarrow C$ ) and inverse sublimation ( $D \rightarrow A$ ). Because we are looking at incremental changes, we can approximate that the processes are reversible, so that the integrand in Eq. (4.2) is zero, i.e.

$$\frac{\delta q}{T} = 0 \tag{4.21}$$

<sup>2</sup>No heat exchange with the external environment

<sup>3</sup>Process takes place without temperature change.

Since no heat is exchanged, entropy change in any reversible adiabatic process is zero. Consequently, the entropy change in the first isothermal process must be of opposite sign to the change in the second isothermal process (Eq.4.3) for our cycle,

$$\frac{\delta q_{BC}}{T_{BC}} = -\frac{\delta q_{DA}}{T_{DA}} \quad (4.22)$$

Now we note that work may be equated to heat in these reversible processes and that the area covered by the circular process as shown in the diagram of Fig. CC is equal to the total work. Note that the work required for the two adiabatic processes needs to be of the same magnitude, but with opposite sign:

$$\Delta v \Delta p = \delta q_{BC} + \delta q_{DA} = \delta q_{BC} \frac{T_{BC} - T_{DA}}{T_{BC}} \quad (4.23)$$

We call the temperature difference in Eq. (4.23)  $dT$  and the pressure difference,  $dp$ , then using Eqs. (4.12 and 4.14) we have

$$\frac{\delta q_{BC}}{T_{BC}} = \frac{L}{T} = \frac{\Delta v dp}{dT} \quad (4.24)$$

Here  $L$  is the latent heat of phase change (Eq. 4.3), or the change in enthalpy that accounts for energy released or absorbed during a change of phase, which occurs without a change of temperature. But note that the latent heat is temperature dependent. We again arrive at the final form of the Clausius Clapeyron equation,

$$\frac{dp}{dT} = \frac{L}{\Delta v T}. \quad (4.25)$$

Integrating for an ideal gas,  $p = \rho R_{wv} T$ , we can arrive at the saturation vapor pressure at a temperature of interest,

$$p = p_o \exp\left[-\frac{L}{R_{wv} T} \left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \quad (4.26)$$

where  $p_o$  is the known pressure of water vapour at a temperature,  $T_o$  and  $R_{wv}$ , is the gas constant for water vapour.

Clausius-Clapeyron deals with phase change at the interface of two phases of the same material, in this case water. However, the Clausius-Clapeyron calculation considers this interface to be over a flat surface. In order to account for the influence of curvature on vapor pressure, the Kelvin equation may be employed. In the case of ice and water vapor, Kelvin's equation may be presented in the form

$$\ln \frac{p}{p_{sat}} = \frac{2\gamma}{r_{curv} R_{wv} T},$$

where  $p$  is vapor pressure,  $p_{sat}$  is saturated vapor pressure,  $r_{curv}$ , the mean curvature,  $R_{wv}$  is the gas constant for water vapor and  $\gamma$  is surface tension.

The mean curvature,  $r_{curv}$ , is described as the average of the principal curvatures (i.e. the maximum,  $r_{max}$ , and minimum,  $r_{min}$ , curvatures) of the surface.

$$r_{curv} = \frac{1}{2} (r_{max} + r_{min}).$$

Then we can write

$$p = p_{sat} \cdot \exp \frac{2\gamma}{r_{curv} R_{wv} T},$$

Then substituting from the Clausius-Clapeyron (Eq 4.26), for saturation vapor pressure,  $p_{sat}$ , we can arrive at an equation for the pressure over a curved ice surface as a function of temperature and pressure.

### 4.3 A crystal in contact with its vapor phase

#### 4.3.1 Molecular view on crystal-vapor interface in equilibrium

To understand the thermodynamics in the vicinity of a crystal vapor interface it often helpful take a microscopic, statistical mechanics perspective which considers individual atoms or molecules. This is particularly useful to comprehend the notion of equilibrium vapor pressure derived previously and to provide foundations for the physics of crystal growth discussed later.

To this end we consider a crystal with vapor in the ambient air at temperature  $T$  as schematically shown in Fig. 4.3.1. On a molecular level, a crystal surface is a highly dynamic state of matter, even in equilibrium. In a given time interval some molecules leave the crystal (desorption, red arrows) while others get incorporated (adsorption, blue arrows). If the red and blue contributions balance exactly, the net flux vanishes and the crystal is said to be in equilibrium with its vapor phase. This is only possible for a particular number density  $c$  of ambient vapor molecules, which is the equilibrium or saturation number density  $c_{sat}$ . If the vapor phase is treated as an ideal gas the equilibrium number density  $c$  can be related to the pressure via the ideal gas law

$$c = \frac{p}{k_B T} \quad (4.27)$$

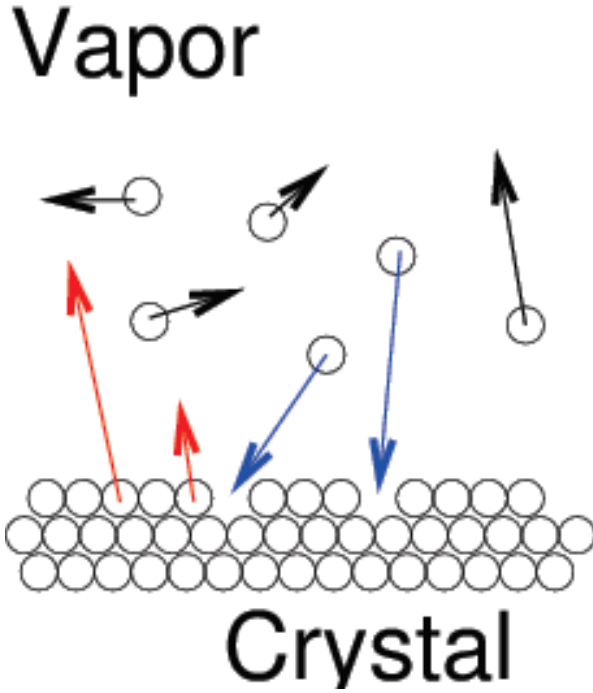
and accordingly the equilibrium number density is related to a (partial) pressure, the equilibrium vapor pressure  $p_{sat}(T) = c_{sat}(T)k_B T$ . If the partial pressure of the ambient vapor attains this value there is no net sublimation or growth of the solid. If there the partial pressure is below the equilibrium value fewer molecules impinge on the crystal leading to sublimation. If the partial pressure is higher than the equilibrium value the crystal is growing. The deviation from equilibrium is often conveniently expressed in terms of the supersaturation  $\sigma$ , a dimensionless measure of the deviation of the vapor pressure or concentration from equilibrium

$$\sigma = \frac{c_{sat} - c}{c_{sat}} = \frac{p_{sat} - p}{p_{sat}} \quad (4.28)$$

#### 4.3.2 Adsorption flux of an ideal gas

In an ideal gas in contact with a solid the flux of molecules impinging the interface can be computed from the distribution of molecular velocities. At temperature  $T$  the probability distribution for the velocity  $\mathbf{v} = (v_x, v_y, v_z)$  of a molecule is given by the Maxwell distribution [?]

$$P(\mathbf{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{m|\mathbf{v}|^2}{2k_B T} \right) \quad (4.29)$$



**Figure 4.2** Schematic of a crystal surface with its ambient vapor phase.

which determines the number of particles per unit volume having a velocity  $\mathbf{v}$ . The number of molecules  $f$  per unit area which approach the interface in unit time from within the vapor phase with arbitrary velocity is given by

$$f = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^0 dv_z c |v_z| p(\mathbf{v}) = c \sqrt{\frac{k_B T}{2\pi m}} \quad (4.30)$$

in terms of the average number density  $c$  of molecules in the gas phase. Using Eq. 4.27, the adsorption flux can be expressed in terms of the ambient partial pressure via

$$f = \frac{p}{\sqrt{2\pi m k_B T}} \quad (4.31)$$

which is known as Knudsen's formula. In equilibrium the desorption flux must balance the adsorption and the desorption flux is only determined by the equilibrium vapor pressure according to

$$f_{sat}(T) = \frac{p_{sat}(T)}{2\pi m k_B T} \quad (4.32)$$

The vapor pressure of a crystal can be envisaged as a measure of volatility. Materials with high vapor pressure such as ice are volatile.

We note that in non-equilibrium the difference between adsorption and desorption flux constitute the amount of material available to move the interface in normal direction with velocity  $v_n$  by growth or sublimation

$$c_{ice} v_n = (f - f_{sat}(T)) \quad (4.33)$$