

# Some useful Statistical Thermodynamics

John Wetlauffer; Notes by Rachel Zammett and Devin Conroy

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## 1 Introduction

We are all familiar with gases, liquid and solids, which make up the 3 possible states of a pure substance. These states of solid, liquid and gas are functions of pressure,  $P$  and temperature,  $T$  as depicted qualitatively in the phase diagram figure 1. The negatively sloped dashed line represents ice in contact with water; the former floating on the latter. There are few other substances with this property and most other materials have a positively sloped solid–liquid coexistence line. Despite substantial advances in our understanding of microscopic phenomena, no phase diagram in its entirety can be computed solely from information about intermolecular interactions; phase diagrams are principally empirically determined.

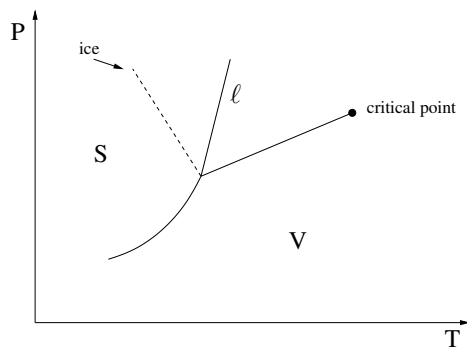


Figure 1: Phase diagram for a pure substance, showing the lines of pressure and temperature delineating the 3 possible phases of matter; gas, liquid and water. The dashed line represents the special case of ice, which has a negatively sloped solid–liquid phase boundary.

## 2 First Law of Thermodynamics

In 1850 Rudolph Clausius first stated what is now referred to as the first law of thermodynamics: the change in internal energy  $E$  of an isolated system is equal to the heat

absorbed by the system  $\delta Q$  minus the work done by the system on its surroundings  $\delta W$ . Mathematically this can be written as

$$dE = \delta Q - \delta W, \quad (1)$$

where the symbol  $\delta$  denotes the path dependence of a differential, namely, that it is an *inexact* differential.

### 3 Second Law of Thermodynamics

Consider an isolated system consisting of two subsystems  $A$  and  $A'$ , as shown in figure 2. The boundary between  $A$  and  $A'$  allows conduction and may move like a piston, but is impermeable to particles i. e. there is no mass transfer across it. We assume that all changes which occur to the system are quasi-static; interactions happen on a long timescale relative to the relaxation time of the system.

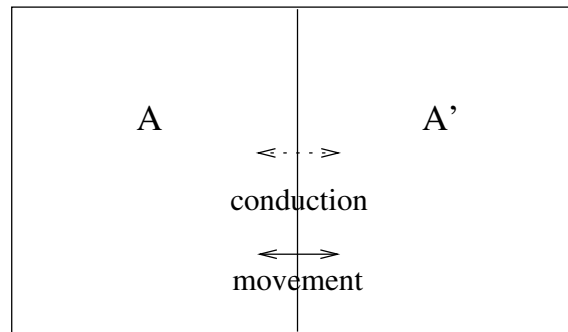


Figure 2: An isolated system consisting of  $A$  adjacent to  $A'$ . Heat conduction is permitted between the subsystems, and the boundary may move as a piston.

The second law states that the number of accessible micro-states of an isolated system,  $\Omega$ , never decreases. If we consider subsystem  $A$  to contain an ideal atomic gas, then the number of accessible micro-states of  $A$  is simply the number of places in space that may be occupied by the gas atoms. Thus,  $A$  has  $\Omega_A$  micro-states and we assume that the volume of  $A$  equals the volume of  $A'$  which contains no gas. We then remove the barrier between  $A$  and  $A'$ . Initially, the system has not relaxed, but at some later time, the whole system  $A + A'$  is available to the gas atoms that were confined to  $A$ .

The probability  $p$  that a particular micro-state is occupied is given by

$$p \propto \frac{\Omega_A}{\Omega_A + \Omega_{A'}}. \quad (2)$$

Moreover, because  $\Omega_A \propto V_A^N$ , where  $V_A$  is the volume of subsystem  $A$  and  $N$  is the number of particles in the system (which is typically of the same order as Avogadro's number,  $6.02 \times 10^{23}$ ). We therefore have that  $p \propto \left(\frac{1}{2}\right)^N$ .

Finally, because the entropy,  $S$ , of a system is defined by

$$S = k_b \ln \Omega, \quad (3)$$

where  $k_b$  is Boltzmann's constant,  $k_b = 1.381 \times 10^{-23} \text{ J K}^{-1}$ . Whence, the second law is written as

$$\Omega_{A'+A} - \Omega_A \geq 0 \Rightarrow dS \geq 0, \quad (4)$$

so that the entropy of a system approaching equilibrium always increases with the equality in equation (4) occurring when the system has reached equilibrium. We can write

$$\delta Q = T dS, \quad (5)$$

thereby demonstrating that  $T$  is an integrating factor for the second law, and hence in the case in which there are no mechanical interactions (no volume change) we find

$$dS_{Total} = dS_A + dS_{A'} = \left( \frac{1}{T_A} - \frac{1}{T_{A'}} \right) \delta Q_A. \quad (6)$$

We therefore see that if  $T_A > T_{A'}$ , heat will flow from  $A$  to  $A'$  until equilibrium is reached.

## 4 Thermodynamic Potentials

Thermodynamic potentials are homogeneous functions that are the principal tools used to understand phase equilibria. They have the following properties

- Thermodynamic potentials have units of energy.
- They all involve the entropy and several, denoted say  $P$ , are such that  $P \propto -S$ .
- For all systems approaching equilibrium,  $dS \geq 0$ , therefore for the potentials  $P$ ,
- for all systems approaching equilibrium,  $dP \leq 0$ : the thermodynamic potential is a minimum.

By way of example, the internal energy of a system,  $E(S, V)$ , satisfies

$$dE = T dS - p dV, \quad (7)$$

and hence is a minimum for constant entropy and volume. The enthalpy of a system,  $H(S, p)$ , is often used when a system is at constant pressure, and is defined by

$$H = E + pV, \quad (8)$$

such that  $dH = 0$  for constant entropy, isobaric processes. The Helmholtz free energy is given by

$$F(V, T) = E - TS, \quad (9)$$

and hence is conserved in an isothermal, constant volume process, while the Gibbs free energy is given by

$$G(T, p) = F + pV = E - TS + pV, \quad (10)$$

From equations (7) and (10), we find

$$dG = -SdT + Vdp, \quad (11)$$

and we note therefore that  $dG = 0$  for systems at constant temperature and pressure.

If we consider a system consisting of a solid in contact with a liquid and we ignore the effect of surface energy, along the solid-liquid phase boundary the phases will have equal free energies, i. e.

$$dG_s = dG_l, \quad (12)$$

where the subscript  $s$  denotes evaluation in the solid and  $l$  evaluation in the liquid. Note that we are considering solid/liquid coexistence and thus pressure and temperature are constrained to a line, defined by  $T_m(p) = p_m(T)$ , due to the Gibbs phase rule. From equations (11) and (12) we can write this as

$$-S_s dT_m + V_s dp = -S_l dT_m + V_l dp, \quad (13)$$

for continuous temperature and pressure across the interface. Rearranging equation (13) gives

$$\frac{dT_m}{dp} = \frac{V_l - V_s}{S_l - S_s} = \frac{T_m}{L}(V_l - V_s). \quad (14)$$

where the latent heat of fusion is  $L$ , and is defined as  $L = \frac{\Delta S}{T_m}$ . In the case of ice, where  $V_l < V_s$ , we see that  $\frac{dT_m}{dp}$  will have negative slope. Hence, from equation (14), we can write the *Clausius-Clapeyron* equation in the following form

$$\frac{dT_m}{dp} = -\frac{T_m}{\rho_s L} \left( 1 - \frac{\rho_s}{\rho_l} \right), \quad (15)$$

where  $\rho_s$  and  $\rho_l$  are the densities of the solid and liquid phases, respectively.

It should be stressed that this treatment only deals with bulk free energies and interfacial and nucleation problems require consideration of the surface energies. This is because the free energy of the system can be shifted due to the surface energy of the phase boundary, intermolecular forces and other effects which extend the equilibrium domain of the liquid phase into the solid region of the bulk phase diagram. In general, for any system in which the surface energy plays a significant role, we can express the total Gibbs free energy as the sum of bulk and surface contributions,

$$G = G_B + G_{surface}, \quad (16)$$

where  $G_B$  represents the bulk free energy and is proportional to the volume of the system and  $G_{surface}$  is proportional to the surface area. Thus, the specific form of the surface area of the solid/liquid interface in question dictates the detailed nature of the shift in equilibrium and thereby leads to the specific effects referred to often in the principal lectures such as the Gibbs-Thomson effect and interfacial premelting. These are reviewed in (1).

## References

- [1] J.G. DASH, A.W. REMPEL AND J.S. WETTLAUFER, *The physics of premelted ice and its geophysical consequences*, Rev. Mod. Phys. **78**, 695 (2006).

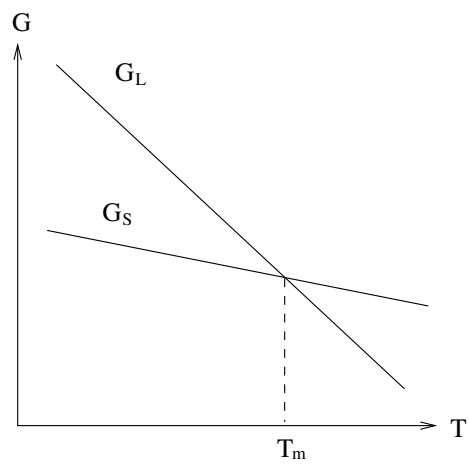


Figure 3: An equilibrium phase diagram of Gibbs free energy  $G$  as a function of temperature  $T$ , where pressure is assumed constant.  $G_L$  denotes the Gibbs free energy associated with the liquid phase;  $G_S$  that associated with the solid phase. We see that below the melting temperature  $T_m$ , the liquid has a greater free energy than the solid, which implies that there is a barrier to forming the solid phase.