

Laws of Thermodynamics

First law

The first law is a statement about conservation of energy. If we let U denote the internal energy of a system, we state that we can decompose this energy change as *heat*, Q and *work*, W .

$$\Delta U = Q \pm W.$$

Note that we use \pm to denote the work, this is because we can define the work both *on* the system or *by* the system, both conventions are used regularly and so care should be taken. The heat is usually defined as the heat *entering* the system.

If the number of particles in a system is constant the instantaneous work done by the system will be

$$dW = PdV,$$

so we have

$$dU = dQ - PdV.$$

Second law

The second law states that the entropy of an isolated system always will increase. Mathematically we can state it as

$$\Delta S \geq T\Delta Q,$$

at least for a constant temperature. For a reversible process, this becomes an equality

$$\Delta S = T\Delta Q \quad (\text{reversible process})$$

This implies that a reversible process is a process that produces no entropy, it is thus a system continuously changing through equilibria states and will therefore often be infinitely slow. A reversible process is thus usually an abstraction, and not a real quality of a process. Processes can however, be close to reversible.

Combining the first and second law gives us the important inequality

$$T\Delta S \geq \Delta U + P\Delta V.$$

For an infinitesimal quantity, this will always be true

$$T dS = dU + P dV.$$

Derivatives of state variables

From the equation

$$dU = T dS - P dV + \mu dN,$$

we get the derivatives

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{V}, \quad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}.$$

Maxwell relations

From the first law we have

$$dU = T dS - P dV. \quad (1)$$

Should therefore express U as a function of S and V , $U = U(S, V)$, can then look at the total derivative of U

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV. \quad (2)$$

Comparing and gives

$$T = \left(\frac{\partial U}{\partial S} \right)_V, \quad P = - \left(\frac{\partial U}{\partial V} \right)_S.$$

Generally

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}.$$

So we get

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V.$$

General state variables

Let us say we have three state variables, X , Y , Z , and we have an equation of state $Z(X, Y)$. We see that Z is not a free variable, but is given by X and Y . Of course, we could have said that X is not the free variable, because it can be given by $X(Y, Z)$, i.e., the equation of state can be solved for any of the three state variables.

The total derivatives of all equation of states become

$$\begin{aligned} dZ &= \left(\frac{\partial Z}{\partial X} \right)_Y dX + \left(\frac{\partial Z}{\partial Y} \right)_X dY, \\ dX &= \left(\frac{\partial X}{\partial Y} \right)_Z dY + \left(\frac{\partial X}{\partial Z} \right)_Y dZ, \\ dY &= \left(\frac{\partial Y}{\partial X} \right)_Z dX + \left(\frac{\partial Y}{\partial Z} \right)_X dZ. \end{aligned}$$

Inserting dY into dX gives

$$\left[\left(\frac{\partial X}{\partial Y} \right)_Z \left(\frac{\partial Y}{\partial X} \right)_Z - 1 \right] dX + \left[\left(\frac{\partial X}{\partial Y} \right)_Z \left(\frac{\partial Y}{\partial Z} \right)_X + \left(\frac{\partial X}{\partial Z} \right)_Y \right] dZ = 0.$$

The differentials are of course independant, so we get

$$\left(\frac{\partial X}{\partial Y} \right)_Z = \left(\frac{\partial Y}{\partial X} \right)_Z^{-1},$$

and

$$\left(\frac{\partial X}{\partial Y} \right)_Z \left(\frac{\partial Y}{\partial Z} \right)_X \left(\frac{\partial Z}{\partial X} \right)_Y = -1.$$

We can now let another state variable be given by X and Y

$$dU = \left(\frac{\partial U}{\partial X} \right)_Y dX + \left(\frac{\partial U}{\partial Y} \right)_X dY.$$

Dividing by dX and holding the equation constant at Z gives

$$\left(\frac{\partial U}{\partial X} \right)_Z = \left(\frac{\partial U}{\partial X} \right)_Y + \left(\frac{\partial U}{\partial Y} \right)_X \left(\frac{\partial Y}{\partial X} \right)_Z$$

Specific Heat

When we add a small amount of heat to a system, the temperature will rise by some small amount, this is the definition of the specific heat of that system. For a given state variable X it is defined as

$$C_X = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta Q}{\Delta T} \right)_X = T \left(\frac{\partial S}{\partial T} \right)_X.$$

Starting at the first law we have

$$TdS = dU + P dV,$$

inserting the complete derivative for dU gives

$$TdS = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + P dV,$$

If we look at the specific heat for a constant volume, we get

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

If we instead keep the pressure constant, we get

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P.$$

This can also be formulated as

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P.$$

Where H is the *enthalpy*:

$$H = U + PV.$$

Equation of State

For most systems all state variables are not independent, but will depend on each other. If we can explicitly give a state variable in terms of the other state variables, that is an equation of state. An example could be the relation

$$P(T, V).$$

The equation of state give important information about how matter will behave under different physical conditions and so is very material dependant.

Ideal gas law

The ideal gas law is an equation of state

$$P = \frac{NkT}{V}, \quad P = kT\rho.$$

Van der Waals Equation of State

The ideal gas presupposes no interaction between the particles. The van der Waals equation of state tries to include some interaction in a basic and approximate manner

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}.$$

Here a and b are parameters describing the particles, b reflects the particles having some volume and a models the attraction between the particles.

Phase Transition

Two phases are in thermodynamic equilibrium, meaning the total entropy

$$S(U, V, N) = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2),$$

is maximized. Taking the total derivative

$$\begin{aligned} dS = & \left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} dU_1 + \left(\frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1} \right)_{U_1, V_1} dN_1 \\ & + \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} dU_2 + \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2, N_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2} \right)_{U_2, V_2} dN_2 \end{aligned}$$

Now, using the fact that $dU_1 = -dU_2$ etc, we can simplify this to

$$\begin{aligned} dS = & \left[\left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} - \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} \right] dU_1 \\ & + \left[\left(\frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} - \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2, N_2} \right] dV_1 \\ & + \left[\left(\frac{\partial S_1}{\partial N_1} \right)_{U_1, V_1} - \left(\frac{\partial S_2}{\partial N_2} \right)_{U_2, V_2} \right] dN_1 \end{aligned}$$

Ensamble

In a microcanonical ensemble, the energy of the system is held constant. All microstates with the given energy are possible and of equal probability. Also known as a NVE -ensemble as the number of particles, volume and energy are constant.

From wikipedia: In simple terms, the microcanonical ensemble is defined by assigning an equal probability to every microstate whose energy falls within a range centered at E . All other microstates are given a probability of zero. Since the probabilities must add up to 1, the probability P is the inverse of the number of microstates W within the range of energy, $P = 1/W$. The range of energy is then reduced in width until it is infinitesimally narrow, still centered at E . In the limit of this process, the microcanonical ensemble is obtained.

Phase space

In general, a system of N particles is described by the particles position and momenta in all dimensions, these evolve in time according to some dynamical equations of the system, so we have

$$q_i = q_i(t, q_0, p_0), \quad p_i = p_i(t, q_0, p_0).$$

Where (q_0, p_0) are the initial conditions of the system. For most systems, the evolution can only be found numerically. A problem then, is that the systems are often chaotic, and so the finite precision in the initial conditions limits our possible solutions.

A goal is to find the average of some quantity over a long time

$$\bar{A} = \frac{1}{T} \int_0^T A(q(t), p(t)) dt.$$

And we will have to include states corresponding to all the parts of phase space visited, however, this requires knowledge of the phase trajectory, which we generally don't have.

A solution put forth by Gibbs is to instead look at phase space as filled by a liquid, the density in phase space is then given by $\rho = \rho(q, p)$ and the number of systems in a volume element $\Delta q \Delta p$ is then given by $\rho(q, p) \Delta q \Delta p$. The greater the density is in a region of phase space, the greater the probability is to find the system in that part of phase space. And so we can now average over the density of the entire phase space to find thermodynamic quantities.

In quantum mechanics, due to the Heisenberg uncertainty principle, a given particle state has the volume

$$d\omega = \frac{d^f q d^f p}{(2\pi\hbar)^f}.$$

We of course choose the density of phase space in a manner that it is normalized in the sense that

$$\int d\omega \rho(q, p) = 1.$$

Ensamble averages are then found from

$$\langle A \rangle = \int \rho(q, p) A(q, p) d\omega.$$

It cannot be proven generally that the time-average, and the ensemble-average found from the density of phase space are equal, and we are now finding the ensemble-average through derivation, but obviously the time-average in experiment. For some systems they can be shown to be equal, but in general we have to simply invoke the ergodic hypothesis that state they are equal.

Liouville's Theorem

To derive the behaviour of the density of phase space we can use the fact that the density of phase space is governed by Hamilton's equations for each point.

Also, no system can make discontinuous jumps in the dynamical variables q and p , and cannot start/stop existing, meaning the equation of continuity applies to the density

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0.$$

Where \vec{J} is the current of system points, which can be expressed as $\vec{J} = \rho \vec{V}$, where \vec{V} is the velocity vector $\vec{V} = (\dot{q}, \dot{p})$. Writing out the nabla operator, we see that we can use Poisson brackets to compactly write the equation of continuity

$$\nabla \cdot \vec{J} = \sum_i \left(\frac{\partial p}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right).$$

Equation of continuity

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0.$$

Now, the phase space density is generally a time-dependant field, $\rho(q, p, t)$ and so the total derivative is

$$\frac{d}{dt} \rho = \frac{\partial \rho}{\partial t} + \{\rho, H\},$$

which we see from the equation of continuity is zero. This is Liouville's theorem. Stated in words it says that the local density of phase space remains constant as seen by an observer moving with a system point.

If we then follow an initial volume element with a constant density, it will remain at a constant volume, but generally change shape as time evolves.

An important consequence of Liouville's theorem is that if ρ is initially constant throughout phase space, meaning all microstates are equally likely. It will remain so as time evolves.

Ergodicity means that the system will eventually visit all of the phase space that is covered by the ensemble, and for ergodic system Liouville's theorem implies that every microstate is equally likely to be visited with time.

Poisson Bracket

In canonical coordinates, the Poisson bracket takes the form

$$\{f, g\} = \sum_{i=1}^N \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right).$$

It has the same role as the commutator has in quantum mechanics.

Any functions, f, g, h of phase space and time follows

- Anticommutativity: $\{f, g\} = -\{g, f\}$
- Distributivity: $\{f + g, h\} = \{f, h\} + \{g, h\}$
- Product rule: $\{fg, h\} = \{f, h\}g + f\{g, h\}$
- If k is time-dependant, but constant over phase space, then $\{f, k\} = 0$.

For canonical coordinates

- $\{q_i, q_j\} = 0$
- $\{p_i, p_j\} = 0$
- $\{p_i, q_j\} = \delta_{ij}$

Using the Poisson bracket, we can write Hamilton's equations as

$$\dot{q} = \{q, H(q, p)\}, \quad \dot{p} = \{p, H(q, p)\}.$$

More generally, for *any* function that is not explicitly dependant on time, but only q and p

$$\frac{d}{dt}f(q, p) = \{f, H\},$$

if there is an explicit time-dependance we have

$$\frac{d}{dt}f(q, p, t) = \{f, H\} + \frac{\partial f}{\partial t}.$$

Microcanonical ensemble

A microcanonical ensemble is completely isolated, and so has constant NVE . The fundamental assumption of statistical mechanics states that all microstates in a microcanonical ensemble are equally likely.

Canonical ensemble

A canonical ensemble is in thermal contact with a reservoir with temperature T . It can therefore exchange energy E with the reservoir, but has NVT constant.

To derive the statistics of the canonical ensemble, we can treat the system-reservoir pair as a microcanonical ensemble, meaning all microstates are equally likely. Let us now assume there is an infinitesimal exchange of energy between the reservoir and the system, we know that

$$dS_R = \frac{1}{T}(dU_R + PdV_R - \mu dN_R).$$

We throw away the dV and dN terms, and so we have

$$S_R(s_2) - S_R(s_1) = \frac{1}{T}[U_R(s_2) - U_R(s_1)] = -\frac{1}{T}[E(s_2) - E(s_1)].$$

Giving

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}.$$

Giving the **Boltzmann factor**

$$e^{-E(s)/kT}.$$

To get an actual probability, we need the normalization constant, giving the **Boltzmann distribution**

$$P(s) = \frac{1}{Z}e^{-E(s)/kT},$$

where

$$Z = \sum_s e^{-E(s)/kT}.$$

The partition function is a constant in the sense that it does not depend on the microstate s , but it does change with the temperature T . In the limit $kT \rightarrow 0$, we see that $Z \rightarrow 1$ as the only contributing state is the ground state as all other possible microstates become suppressed. As kT increases, Z grows, as more microstates become available to the system. If we shift all energies by a constant factor of E_0 , the partition function picks up a factor $e^{-E_0/kT}$, but it is inconsequential as it cancels out when calculating the probabilities $P(s)$.

Using the Boltzmann distribution, we can find expectancies as

$$\bar{X} = \sum_s X(s)P(s) = \frac{1}{Z} \sum_s X(s)e^{-\beta E(s)}.$$

For energy we find

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z.$$

To find other quantities, we can calculate the Helmholtz free energy

$$F = -kT \ln Z.$$

Giving us

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

Other

$$e^{\hbar\omega/kT} \simeq 1 + \frac{\hbar\omega}{kT}, \quad T \gg \hbar\omega/k.$$

Stirling's approximation

Coarse

$$\log n! = n \log n - n,$$

Fine

$$n! = \sqrt{2\pi n} n^n e^{-n}.$$

Constants

Boltzmann's constant	$k = 1.381 \times 10^{-23} \text{JK}^{-1}$
Avogadro's Number	$N_{\text{A}} = 6.023 \times 10^{23} \text{mol}^{-1}$
$k \cdot N_{\text{A}}$	$R = 8.314 \text{JK}^{-1} \text{mol}^{-1}$

Einstein Solid

The Einstein solid is an attempt to describe the vibrations of the atoms in a regular lattice, it is based on two fundamental assumptions

- Each atom in the lattice is an *independent* 3D quantum harmonic oscillator
- All atoms oscillate with the same common frequency (this is the big contrast with the Debye model)

Assuming we are looking at a lattice containing N atoms, the first assumption tells us we have $3N$ degrees of freedom, as each atom can vibrate in three independent directions. Each oscillator will be occupied by certain number of phonons, which are the quanta in lattice vibrations as photons are the quanta in electromagnetic oscillations. Phonons are bosons with no chemical potential ($\mu = 0$) so the Bose-Einstein distribution predicts that the average number of phonons per oscillator will be

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/kT} - 1}.$$

As each phonon carries the energy $\hbar\omega$, we find the average energy per oscillator to be

$$\langle \epsilon \rangle = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}.$$

Summing over all the degrees of freedom of the system gives the total internal energy as

$$U = \frac{3N\hbar\omega}{e^{\hbar\omega/kT} - 1}.$$

We can now find the specific heat

$$C_V = 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2}.$$

We now introduce the characteristic Einstein temperature $T_E = \hbar\omega/k$ and we simplify the expression for the specific heat in the limits $T \ll T_E$ and $T \gg T_E$

$$C_V = \begin{cases} 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 e^{-\hbar\omega/kT}, & T \ll T_E, \\ 3Nk, & T \gg T_E. \end{cases}$$

When the temperature is high, we recover the Dulong-Petit law that predicts a constant heat capacity in agreement with the equipartition principle. However, when $T \rightarrow 0$ we see that $C_V \rightarrow 0$ as required by the third law, however, it goes to zero exponentially, while experiment shows that it should go as $C_V \propto T^3$.

Debye Theory of Solids

Instead of treating every atom as an independent harmonic oscillator, we instead focus on the phonons and treat it as a ‘phonon gas in a box’ (the box being the solid). The energy of a phonon is

$$\epsilon_n = \hbar\omega_n = \hbar vk_n = \frac{\hbar\pi v}{L}n,$$

where n is the mode of the phonon and v is the speed of sound in the solid. The phonons follow a Bose-Einstein distribution, so the average energy of phonons in mode n is then

$$\langle\epsilon_n\rangle = \frac{\epsilon_n}{e^{\epsilon_n/kT} - 1}$$

Unlike for a photon gas, there is a minimum wavelength the phonon can have (two times the lattice spacing) and thus a maximum mode. For a cubic box, it will be $N_{\max} = \sqrt[3]{N}$ and so the total energy of all the phonons in the solid is

$$U = 3 \sum_{n_x=1}^{\sqrt[3]{N}} \sum_{n_y=1}^{\sqrt[3]{N}} \sum_{n_z=1}^{\sqrt[3]{N}} \langle\epsilon_n\rangle.$$

Where we have multiplied the result by three, since sound waves can have three independent polarizations.

Assuming L is macroscopic, the density of modes will be very high, and we can change the sums into an integral. The three sums is actually a sum over a cubic box in N -space, but it will be simpler to instead integrate over an eighth-sphere with the same volume. The volume of the box is N and so the sphere needs to have a radius of

$$n_{\max} = \left(\frac{6N}{\pi}\right)^{1/3}.$$

The angular integral will give $\pi/2$, so the total energy can then be written as

$$U = \frac{3\pi}{2} \int_0^{n_{\max}} n^2 \langle\epsilon_n\rangle \, dn.$$

Inserting the average energy gives

$$U = \frac{3\pi}{2} \int_0^{n_{\max}} \frac{\hbar\pi v}{L} n^3 \frac{1}{e^{\hbar\pi vn/LkT} - 1} \, dn.$$

We now do the substitution $x \equiv \hbar\pi vn/LkT$.

$$U = \frac{3\pi}{2} \frac{\hbar\pi v}{L} \left(\frac{LkT}{\hbar\pi v}\right)^4 \int_0^{x_{\max}} \frac{x^3}{e^x - 1} \, dx.$$

Where

$$x_{\max} = \frac{\hbar\pi v}{LkT} \left(\frac{6N}{\pi}\right)^{1/3} \equiv \frac{T_D}{T},$$

where we introduced the Debye temperature

$$T_D = \frac{\hbar\pi v}{Lk} \left(\frac{6N}{\pi}\right)^{1/3}.$$

We then have the total energy

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T/T_D} \frac{x^3}{e^x - 1} dx.$$

The integral can only be solved numerically. However, in the limits $T \ll T_D$ and $T \gg T_D$ we can simplify it.

When $T \gg T_D$ the upper limit of the integral is much less than 1, and $x \ll 1$ so that $e^x \simeq 1 + x$. This gives

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T/T_D} x^2 dx = \frac{9NkT^4}{T_D^3} \frac{T^3}{3T_D^3} = 3NkT.$$

Which recovers the Dulong-Petit law

$$C_V = 3Nk.$$

When $T \ll T_D$, the upper limit is very large. The exponential in the denominator effectively kills the integrand when x becomes large, so replacing the upper limit with ∞ introduces little error, giving

$$U = \frac{9NkT^4}{T_D^3} \int_0^\infty x^2 dx = \frac{9NkT^4}{T_D^3} \frac{\pi^4}{15} = \frac{3\pi^4}{5} \frac{NkT^4}{T_D^3}.$$

Giving the heat capacity

$$C_V = \frac{12\pi^4}{5} \left(\frac{T}{T_D} \right)^3 Nk.$$

Which gives us the Debye T^3 law.

At $T = T_D$ the heat capacity has reached 95 % of it's maximum value, so as long as $T > T_D$ we can use the equipartition theorem without much trouble. Although the Debye temperature can be calculated from speed of sound in a solid using the definition, it is more common to choose the T_D that makes the theoretical prediction best fit the measured heat capacity.

Bose-Einstein Condensation

We now turn to gases of bosons where the chemical potential is *not* zero. Considering the system as $T \rightarrow 0$, we know that more and more particles will settle into the ground state. Looking at a boson gas in a L^3 box, the ground state will have energy

$$\epsilon_0 = \frac{p^2}{2m} = \frac{\hbar^2 k_0^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}(1+1+1) = \frac{3\hbar^2 \pi^2}{2mL^2}.$$

At any temperature, the system follows the Bose-Einstein distribution, so the number of particles in the ground state will be

$$N_0 = \frac{1}{e^{(\epsilon_0 - \mu)/kT} - 1}.$$

So we see that $\mu < \epsilon_0$ and $\mu \rightarrow \epsilon_0$ when $T \rightarrow 0$. In this limit, we can simplify the exponential

$$N_0 = \frac{kT}{\epsilon_0 - \mu}.$$

Now, we would be finished if we only knew μ as a function of T , but we don't. However, we do have a condition that can determine it

$$\sum_s \frac{1}{e^{\epsilon_s - \mu/kT} - 1} = N.$$

To use this condition, we transform it into an integral, this is valid when $kT \gg \epsilon_0$ so that the density of modes is high. Using the density of states

$$g(\epsilon) = \frac{2}{\sqrt{\pi}} \left(\frac{m}{2\pi\hbar^2} \right)^{3/2} V \sqrt{\epsilon}.$$

It is half that of the electron gas, as the electron gas has two spin orientations.

$$N = \int_0^\infty g(\epsilon) \frac{1}{e^{(\epsilon - \mu)/kT} - 1} d\epsilon.$$

If we assume that $\mu = 0$ we get

$$N = 2.612 \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} V.$$

Which can only be true for a single temperature T , we call this temperature T_C

$$kT_c = 0.527 \frac{2\pi\hbar^2}{m} \left(\frac{N}{V} \right)^{2/3}.$$

For temperatures $T > T_C$, we find $\mu < 0$, while for $T < T_C$ we find

$$N_{\text{excited}} = 2.612 \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} V = N \left(\frac{T}{T_C} \right)^{3/2}, \quad (T < T_C).$$

Thermodynamic potentials

To create a system from vacuum, we would need to supply the system's internal energy U . However, to make room for it in the environment, we also need to provide the work PV , where P is the (constant) pressure of the environment, and V is the total volume of the system. We define the *enthalpy* to be

$$H \equiv U + PV.$$

However, since the system will have some entropy S , it can absorb some energy from its surroundings as heat to bring it to the same temperature. If the environment is at constant temperature T , the system will get the energy TS for free, so the energy of the system is best described by *Helmholtz' free energy*

$$F \equiv U - TS.$$

If we also include the PV -term, i.e., the cost of making room for the system, we have *Gibb's free energy*

$$G \equiv U - TS + PV.$$

So we see that $G = F + PV = H - TS$. We can summarize the results as follows

$$\begin{array}{c} \uparrow \\ -TS \left| \begin{array}{|c|c|} \hline F & G \\ \hline U & H \\ \hline \end{array} \right. \\ \hline +PV \rightarrow \end{array}$$

Now, in an isolated system, we know that the entropy always increases and will be maximized over long time scales. However, if we look at a system that is not isolated, but is in contact with a heat bath at constant temperature, the Helmholtz free energy of that system will be minimized. This is because the entropy of the system and reservoir combined will be maximized. Looking at the expression for the free energy $F = U - TS$, we see that the entropy of the system counts negative as expected, while the energy is positive. This is because the system will introduce entropy in the reservoir if it gives up energy to it, this is especially true at low temperatures T as the entropy change per unit energy is proportional to $\frac{1}{T}$. Likewise, the Gibbs free energy is minimized for a system that has constant pressure and temperature, but can change volume and energy by interacting with its environment

- At constant energy and volume (isolated system) entropy increases.
- At constant volume and temperature Helmholtz' free energy decreases.
- At constant pressure and temperature Gibbs' free energy decreases.

In all three cases we assume that N is held constant. So that $NVE \rightarrow S \uparrow$, $NVT \rightarrow F \downarrow$, $NPT \rightarrow G \downarrow$. If we want to include material contact, we use the *grand free energy*: $\Phi \equiv U - TS - \mu N$.

Thermodynamic identities

(Write out the total differential, and then substitute in for dU .)

$$\begin{aligned}dU &= T dS - P dV + \mu dN, \\dH &= T dS + V dP + \mu dN, \\dF &= -S dT - P dV + \mu dN, \\dG &= -S dT + V dP + \mu dN.\end{aligned}$$

From these we find many important partial derivatives, for example

$$\begin{aligned}S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N}, & P &= -\left(\frac{\partial F}{\partial V}\right)_{T,N}, & \mu &= \left(\frac{\partial F}{\partial N}\right)_{T,V} \\S &= -\left(\frac{\partial G}{\partial T}\right)_{P,N}, & V &= \left(\frac{\partial G}{\partial P}\right)_{T,N}, & \mu &= \left(\frac{\partial G}{\partial N}\right)_{T,P}\end{aligned}$$

Here we assume there's only one kind of particle, if there are more we replace μdN with $\sum_i \mu_i dN_i$.

1 Phase Transition

We consider an isolated system of two phases in thermodynamic equilibrium, we know the total entropy will be maximized spontaneously

$$S(U, V, N) = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2).$$

Giving the total change in S to be (in each partial derivative, the two free variables are held constant)

$$dS = \left[\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} \right] dU_1 + \left[\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right] dV_1 + \left[\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} \right] dN_1.$$

Now, if the system is at thermal equilibrium, we know that $dS = 0$ is zero for any change in U_1 , V_1 and N_1 independently, meaning all the coefficients have to be independent. Using the thermodynamic identity we have

$$\left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V} \right)_{U,N} = \frac{P}{T}, \quad \left(\frac{\partial S}{\partial N} \right)_{U,V} = -\frac{\mu}{T}.$$

So we see that the equilibrium conditions are

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2.$$

Clausius-Clapeyron

We now consider the slope of the phase boundary between two co-existing phases. If we want to move along the curve, we will generally have to change the pressure and temperature in the right way in relation to each other, so that dP and dT . The equilibrium condition then gives

$$G_g = G_l \quad \Rightarrow \quad -S_g dT + v_g dP = -S_l dT + v_l dP.$$

Which gives the slope

$$\left(\frac{dP}{dT} \right) = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T\Delta V}.$$

Where L is the *latent heat*. Note that L and ΔV are both extensive, so the slope of the phase boundary must be an intensive quantity.

Entropy

Entropy is given by

$$S = k \log \Omega.$$

Where Ω is the multiplicity, i.e., the number of microstates the system can inhabit.

For substances with $S_0 = 0$ (Sometimes referred to as the third law, but is not universally true), we can find $S(T)$ as

$$S(T) = \int_0^T \frac{C_P(T)}{T} dT,$$

for this to be valid, we must have

$$\lim_{T \rightarrow 0} C_P(T) = 0.$$

At phase transitions, we also have a finite, discontinuous jumps, which will be proportional in size to the latent heats of the phase transitions. So just at above the boiling temperature for a substance, we can for example find the entropy as

$$S(T_b) = S_s(0 \rightarrow T_m) + \frac{\Lambda_m}{T_m} + S_l(T_m \rightarrow T_b) + \frac{\lambda_B}{T_b \lambda}.$$

Extensivity and Intensivit

- **Extensive:** V, N, S, H, U, F, G
- **Intensive:** T, P, μ, ρ

Extensive times intensive is extensive. Extensive divided by extensive is intensive. Extensive times extensive is neither. Extensive plus extensive is extensive and likewise for intensive, extensive plus intensive is *not allowed*.

Third law of thermodynamics

The third law states that as $T \rightarrow 0$, the entropy must tend to some constant number $S(0) = S_0$. Sometimes the third law is formulated as $S \rightarrow 0$, but this is not universally true, as there are some systems with a degenerated ground state. However, the specific heat capacity can be formulated as

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial U}{\partial S} \right)_V \left(\frac{\partial S}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial S}{\partial \ln T} \right)_V.$$

And as $S \rightarrow \text{const}$ as $T \rightarrow 0$ and $\ln T \rightarrow \infty$, we see that $C_V \rightarrow 0$. (The same is true for C_P).

We see that this must be the case from the fact that

$$S_f - S(0) = \int_0^{T_f} \frac{C_V}{T} dT.$$

If C_V does not go to zero as $T \rightarrow 0$ we see that the denominator causes the integral to diverge, and as $S(0)$ has to be finite, it would imply that S_f diverges, which is clearly not the case.

Response Functions

Specific heats are just one example of response functions

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad C_P = \left(\frac{\partial H}{\partial T} \right)_P.$$

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P.$$

$$C_X = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta Q}{\Delta T} \right)_X = T \left(\frac{\partial S}{\partial T} \right)_X.$$

Other response functions are compressibilities

$$K_X = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_X.$$

And thermal expansion coefficient

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P.$$

All these response functions are related and one can show that

$$C_P - C_V = \frac{TV}{K_T} \alpha^2.$$

$$K_T - K_S = \frac{TV}{C_P} \alpha^2.$$

and

$$\frac{C_P}{C_V} = \frac{K_T}{K_S}.$$

For magnetic systems, the susceptibilities play the same roles as the compressibilities.