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 regurarly 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

$$\mathrm{d}W = P\mathrm{d}V,$$

so we have

$$\mathrm{d}U = \mathrm{d}Q - P\mathrm{d}V.$$

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 continously changing through equilibria states and will therefore often be infinitely slow. A reversible process is thus ususally 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

$$T\,\mathrm{d}S = \mathrm{d}U + P\,\mathrm{d}V.$$

Derivatives of state variables

From the equation

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}N,$$

we get the derivatives

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

Maxwell relations

From the first law we have

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V. \tag{1}$$

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

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V. \tag{2}$$

Comparing and gives

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

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

$$\mathrm{d}Z = \left(\frac{\partial Z}{\partial X}\right)_Y \mathrm{d}X + \left(\frac{\partial Z}{\partial Y}\right)_X \mathrm{d}Y,$$

$$\mathrm{d}X = \left(\frac{\partial X}{\partial Y}\right)_Z \mathrm{d}Y + \left(\frac{\partial X}{\partial Z}\right)_Y \mathrm{d}Z,$$

$$\mathrm{d}Y = \left(\frac{\partial Y}{\partial X}\right)_Z \mathrm{d}X + \left(\frac{\partial Y}{\partial Z}\right)_X \mathrm{d}Z.$$

Inserting $\mathrm{d}Y$ into $\mathrm{d}X$ gives

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

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 temprature 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

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

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

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

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

$$\mathrm{d}S = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1, N_1} \mathrm{d}U_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1, N_1} \mathrm{d}V_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{U_1, V_1} \mathrm{d}N_1$$
$$+ \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2, N_2} \mathrm{d}U_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2, N_2} \mathrm{d}V_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U_2, V_2} \mathrm{d}N_2$$

Now, using the fact that $\mathrm{d}U_1 = -\mathrm{d}U_2$ etc, we can simplify this to

$$\mathrm{d}S = \left[\left(\frac{\partial S_1}{\partial U_1}\right)_{V_1, N_1} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2, N_2}\right] \mathrm{d}U_1$$
$$+ \left[\left(\frac{\partial S_1}{\partial V_1}\right)_{U_1, N_1} - \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2, N_2}\right] \mathrm{d}V_1$$
$$+ \left[\left(\frac{\partial S_1}{\partial N_1}\right)_{U_1, V_1} - \left(\frac{\partial S_2}{\partial N_2}\right)_{U_2, V_2}\right] \mathrm{d}N_1$$

Ensambles

In a microcanonical ensamble, 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-ensamble 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

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

Where (q_0, p_0) are the inital 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

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

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 the 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

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

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

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

Ensamble averages are then found from

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

It cannot be proven generally that the time-average, and the ensamble-average found from the density of phase space are equal, and we are now finding the ensamble-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 goverened by Hamilton's equations for each point.

Also, no system can make discontinious jumps in the dynamical variables q and p, and cannot start/stop exisiting, 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 $\vec{V} = (\dot{\vec{q}}, \dot{\vec{p}})$. Writing out the nabla operator, we see that we can use Poisson brackets to compactily 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

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

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

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

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 Liouvilles 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 cannonical 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

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

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

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

Microcannonical ensamble

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

Ergodic hypothesis

States that over long time periods, the time spent by a system in some region of phase space, i.e., in given microstates, with the same energy is proportional to the volume of that region. Stated simpler: All accesible microstates are equiprobable over long periods of time.

Liouville's Theorem

States that for Hamiltonian systems, the local density of microstates following a particle path through phase space is constant as viewed by an observer moving with the ensamble.

ma where $D\rho/Dt$ is the material or total derivative, it gives the change in ρ seen by a particle moving with the flow.

Lioville's theorem shows that flow in phase space is conservative and the microcannonical ensamble must be time independent. (If phase space is of uniform density, then it will stay so forever).

Note that the ergodic hypothesis is one specific solution to the Liouville theorem equation, in fact, it is the simplest.

Cannonical ensamble

A cannonical ensamble 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 cannonical ensamble, we can treat the system-reservoir pair as a microcannonical ensamble, meaning all microstates are equally likely. Let us now assume there is a infinitesimal exchange of energy beween the reservoir and the system, we know that

$$\mathrm{d}S_\mathrm{R} = \frac{1}{T}(\mathrm{d}U_\mathrm{R} + P\mathrm{d}V_\mathrm{R} - \mu\mathrm{d}N_\mathrm{R}).$$

We throw away the $\mathrm{d}V$ and $\mathrm{d}N$ terms, and so we have

$$S_\mathrm{R}(s_2) - s_\mathrm{R}(s_1) = \frac{1}{T}[U_\mathrm{R}(s_2) - U_\mathrm{R}(s_1)] = -\frac{1}{T}[E(s_2) - E(s_1)].$$

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 $kT \to 0$, we see that $Z \to 1$ as the only contributing state is the ground state as all other possible microstates become supressed. 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

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

For the energy this can be written convieniently as

$$\langle E \rangle = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)} = \frac{1}{Z} \sum_s \frac{\partial}{\partial \beta} e^{-\beta E(s)}.$$

Giving

$$\langle E \rangle = \frac{1}{Z} \frac{\partial Z}{\partial \beta}.$$

Which can again be rewritten as

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z.$$

For the energy squared, we get

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}.$$

Which can be rewritten as

$$\langle E^2 \rangle = \frac{\partial^2}{\partial \beta^2} \ln Z + \left[\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right]^2 = \frac{\partial^2}{\partial \beta^2} \ln Z + \left[\frac{\partial}{\partial \beta} \ln Z \right]^2 = \frac{\partial^2}{\partial \beta^2} \ln Z + \langle x \rangle^2.$$

And so the variance is easily written as

$$\langle \Delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Z.$$

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

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

Giving us

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

Other

$$e^x \simeq 1 + x, \qquad x \ll 1.$$

$$\ln(1 - x) \approx -x, \qquad x \ll 1.$$
$$(1 - x)^k \approx 1 - kx, \qquad x \ll 1.$$

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

Stirling's approximation

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

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

Constants

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

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 *independant* 3D quantum harmonic oscialltor

- 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 assumptions tells us we have $3N$ degrees of freedom, as each atom can vibrate in three independant 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 $T \gg T_E$

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

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

Debye Theory of Solids

Instead of treating every atom as an independant 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

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

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 independant 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 eigth-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

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

Inserting the average energy gives

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

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

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

Where

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

where we introudced the Debye temperature

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

We then have the total energy

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

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

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

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

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

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. Altough the Debye temperature can be calculated from speed of sound in a solid using the defintion, 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 $T \to 0$, 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 distibution, 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 $\mu \to \epsilon_0$ when $T \to 0$. 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

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

Thermodynamic potentials

To create a system from vacuum, we would need to suply the systems 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 it's surrounding 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

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

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 Gibb's free energy is minimized for a system that has constant pressure and temperature, but can change volume and energy by interacting with it's environment

- At constant energy and volume (isolated system) entropy increases.

- At constant volume and temperature Helmholtz' free energy decreases.

- At constant pressure and temperature Gibb's free energy decreases.

In all three cases we assume that N is held constant. So that $NVE \to S \uparrow$, $NVT \to F \downarrow$, $NPT \to G \downarrow$. 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.)

$$dU = T \, dS - P \, dV + \mu \, dN,$$
$$dH = T \, dS + V \, dP + \mu \, dN,$$
$$dF = -S \, dT - P \, dV + \mu \, dN,$$
$$dG = -S \, dT + V \, dP + \mu \, dN.$$

From these we find many importan partial derivatives, for example

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

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

Here we assume there's only one kind of particle, is there are more we replace $\mu \, dN$ 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)

$$\mathrm{d}S = \left[\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2}\right] \mathrm{d}U_1 + \left[\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}\right] \mathrm{d}V_1 + \left[\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right] \mathrm{d}N_1.$$

Now, if the system is at thermal equilbrium, we know that $\mathrm{d}S = 0$ is zero for any change in U_1, V_1 and N_1 independently, meaning all the coefficients have to be independant. Using the thermodynamic indentity we have

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

So we see that the equilbrium conditions are

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

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 $\mathrm{d}P$ and $\mathrm{d}T$. The equilibrium condition then gives

$$G_g = G_l \qquad \Rightarrow \qquad -S_g \, \mathrm{d}T + v_g \, \mathrm{d}P = -S_l \, \mathrm{d}T + v_l \, \mathrm{d}P.$$

Which gives the slope

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

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

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

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for this to be valid, we must have

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

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

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

The Gibbs entropy formula states

$$S = -k \sum_s P_s \ln P_s.$$

It is valid for both the microcanonical and canonical ensambles.

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 $T \to 0$, the entropy must tend to some constant number $S(0) = S_0$. Sometimes the third law is formulated as $S \to 0$, 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 $S \to$ const as $T \to 0$ and $\ln T \to \infty$, we see that $C_V \to 0$. (The same is true for C_P).

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

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

If C_V does not go to zero as $T \to 0$ 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

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

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

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

Other response functions are compressibilities

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

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.

Fluctations

We find expectencies from the Boltzmann distribution from

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

This gives us

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z.$$

And

$$\langle E^2 \rangle = \frac{\partial^2}{\partial \beta^2} \ln Z + \left[\frac{\partial}{\partial \beta} \ln Z \right]^2 = \frac{\partial^2}{\partial \beta^2} \ln Z + \langle x \rangle^2.$$

And so

$$\langle \Delta E^2 \rangle = \frac{\partial^2}{\partial \beta^2} \ln Z.$$

Heat capacity is given by

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

And so from $\langle E \rangle$ we find

$$C_V = -\frac{\partial}{\partial T} \frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta} \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \ln Z = \frac{1}{kT^2} \frac{\partial^2}{\partial \beta^2} \ln Z.$$

Comparing $\langle \Delta E^2 \rangle$ to C_V gives

$$\langle \Delta E^2 \rangle = kT^2 C_V.$$

Note that C_V is proportional to N, so it follows that the energy fluctuations of a system is proportional to the number of particles in that system. However, as the total energy is also proportional to N, i.e., $\langle E \rangle \propto N$, it follows that the *relative* energy fluctuations of the system are inversely proportional to the square root of the number of particles:

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{\langle E \rangle} \propto \frac{1}{\sqrt{N}}.$$

If we look at a NVT ensamble, the 'constant temperature' is the temperature of the heat bath and so the system does actually have temperature fluctuations (in comparison, a NVE ensamble has no fluctuation in energy). Assuming the system has an instantaenous energy fluctuation, it will lead to a temperautre change given by

$$\Delta T = \Delta E \left(\frac{\partial T}{\partial E} \right)_{N,V} = \frac{\Delta E}{C_V}.$$

And so the mean square fluctuations in temperature will be

$$\langle \Delta T \rangle = \frac{\langle \Delta E^2 \rangle}{C_V^2} = \frac{kT^2}{C_V}.$$

So the mean square temperature fluctuations are inversely proportional to N. However, unlike the total energy, the temperature of the system is an intensive size and independent of N, so the relative temperature fluctuations will also be inversely proportional to the square root of the number of particles

$$\frac{\sqrt{\Delta T^2}}{T} \propto \frac{1}{\sqrt{N}}.$$

Equipartition Theorem

The equipartition theorem states that any quadratic degree of freedom will carry an average energy of $kT/2$ when the system is in equilibirum. As an example, consider the ideal gas, which only has the kinetic energy of the gas particles (as the particles are non-interacting), the hamiltonian will be

$$H = \sum_{i=1}^{N} \frac{1}{2} m(v_{ix}^2 + v_{iy}^2 + v_{iz}^2),$$

and so the average kinetic energy of the ideal gas will be

$$U = \frac{3}{2} NkT,$$

at thermal equilibrium. Which leads to the law of Dulong-Petit that $C_V = 3Nk$ for an ideal gas.

The equipartition theorem breaks down at low temperature as the discrete nature of energy levels, i.e, start to matter. The equipartition theorem only applies when in the high-temperature limit where the spacing between energy levels is much less than kT.

Random Walker

The symmetric walker is given by uncorrelated steps to the left and right with the same probability $p = q$ and often we start the particle in the origin $x_0 = 0$.

$$x_N = \sum_{i=1}^{n} \delta x_i.$$

We find the expectation as a difference equation, we have

$$x_{i+1} = x_i + \delta x_i.$$

Inserting for the step δx_i gives

$$x_{i+1} = \begin{cases} x_i + a & \text{with probability } p, \\ x_i - a & \text{with probability } q, \end{cases}$$

So we have

$$\langle x_{i+1} \rangle = p(\langle x_i \rangle + a) + q(\langle x_i \rangle - a) = \langle x_i \rangle + (p - q)a.$$

If $p = q = 1/2$ we get

$$\langle x_{i+1} \rangle = \langle x_i \rangle \qquad \Rightarrow \qquad \langle x_n \rangle = x_0 = 0.$$

Now we calculate the expectany of the square displacement, we have

$$x_{i+1}^2 = x_i^2 + 2x_i\delta x_i + \delta x_i^2.$$

Inserting for δx_i gives

$$x_{i+1}^2 = \begin{cases} x_i^2 + 2x_i a + a^2 & \text{with probability } p, \\ x_i^2 - 2x_i a + a^2 & \text{with probability } q, \end{cases}$$

so the expectancy becomes

$$\langle x_{i+1}^2 \rangle = \langle x_i^2 \rangle 2(p - q)a\langle x_i \rangle + a^2.$$

For the symmetric walker $(p = q)$ we then get

$$\langle x_{i+1}^2 \rangle = \langle x_i^2 \rangle + a^2 \qquad \Rightarrow \qquad \langle x_n^2 \rangle = na^2.$$

Which we can write as the linear diffusion

$$\langle x \rangle(t) = 2Dt,$$

for $D = a^2/\Delta t$.

Central Limit Theorem

Let X be a stochastic variable that follows a distribution with a well-defined mean μ and finite variance σ^2. Then if take many indenpendant samples of X: $\langle x_i \rangle_{i=1}^N$. The central limit theorem states that as N grows large, the sum of the samples $\sum_i x_i$ will follow a normal distribution. The distribution being sampled is often referred to as the *parent distribution* and does not have to resemble a normal distribution.

To be more specific, if we calculate the sample average

$$\bar{X} = \frac{\sum_{i=1}^N X_i}{N}.$$

Then $\bar{X}$ is also a stochastic variable. The expectancy of $\bar{X}$ will obviously be the mean μ by the law of large numbers. The CLT however, also guarantees that $\bar{X}$ will be (approximately) normal distributed with variance σ^2/n. If we instead of taking the sample average just take the sample sum,

$$S_n = \sum_{i=1}^N X_i,$$

then the mean will be $N\mu$ and the variance will be $N\sigma^2$. If we want a $N(0, \sigma^2)$ distribution we can study $\sqrt{N}(S_n - \mu)$. And if we a standard normal distribution, we can study

$$\frac{\sqrt{N}(S_n - \mu)}{\sigma}.$$

Langevin Equation

Ikke pensum?

Magnetic Systems

When looking at magnetic systems, the magnetic moment of particles can be aligned with or against a magnetic field, which will lead to work. This means the particle or system can perform work by changing their magnetization (or rather, the direction of their magnetization). We reflect this by changing the pressure-work to magnetic-work

$$\mathrm{d}W = P\,\mathrm{d}V \quad \to \quad \mathrm{d}W = B\,\mathrm{d}M.$$

Both P and M are intensive, while V and M are extensive, so this change makes sense. It follows that

$$\mathrm{d}U = T\,\mathrm{d}S + B\,\mathrm{d}M.$$

And from this identity we can derive many new partial derivatives

$$T = \left(\frac{\partial U}{\partial S}\right)_M, \qquad B = \left(\frac{\partial U}{\partial M}\right)_S,$$

we can also find new Maxwell relations.

The enthalpy no changes to

$$H(S, B) = U - BM.$$

And the free energy becomes

$$F(T, M) = U - TS.$$

And so we get

$$\mathrm{d}F = -S\,\mathrm{d}T + B\,\mathrm{d}M,$$

giving

$$S = -\left(\frac{\partial F}{\partial T}\right)_M, \qquad B = \left(\frac{\partial F}{\partial M}\right)_T,$$

And similar for the Gibbs free energy

$$G = U - BM - TS, \qquad \mathrm{d}G = -M\,\mathrm{d}B - S\,\mathrm{d}T.$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_B, \qquad M = \left(\frac{\partial G}{\partial B}\right)_T,$$

The *susceptibility* is the change in magnetization as a result of the change in field

$$\chi = \left(\frac{\partial M}{\partial B}\right)_T.$$

And we also define the speffic heat

$$C_B = \left(\frac{\partial H}{\partial T}\right)_B.$$

Magnetic materials

The interaction energy between a magnetic material and a magnetic field is given by $U_B = -MB$ and for weak fields, we can write the induced magnetic moment as $M = \chi B$. We divide materials into three classes. Diagmagnetic materials have negative susceptibilites, $\chi < 0$, and so the induced magnetic moment will increase the energy of the system, thus we must perform work to move the material into the magnetic field (diamagnetic materials are repelled by magnetic fields). Paramagnetic materials however, have positive susceptibilities, $\chi > 0$, and are thus attracted to magnetic fields. Paramagnetic materials that retain the induced magnetization even when removed from the external field are referred to as *ferromagnetic*.

Paramagnets

In an ideal paramagnet, every dipole will only react with the external magnetic field, and will not interact directly with it's closest neighbors. In most paramagnetic crystals, the interaction with neighboring atoms can be ignored without introducing to much error. Every dipole will then get an energy eigenvalues

$$\epsilon_m = -g\mu_B B m, \quad m = -J, -J+1, \ldots, J-1, J.$$

The partition function becomes

$$Z = \sum_{m=-J}^{J} e^{\beta g \mu_B B M}.$$

This is a geometric series and evaluates to

$$Z = \frac{e^{(J+1)a} - e^{-aJ}}{e^a - 1} = \frac{\sinh \frac{2J+1}{2J}}{\sinh \frac{x}{2J}}.$$

Where $x = \beta g \mu_B B J$. And from this the Gibbs free energy follows $G = -kT \log Z$, and so we find the expectency for the magnetization of a single dipole to be

$$m = \langle \hat{m}_z \rangle = -\frac{\partial G}{\partial B} = g\mu_B J B_J(x).$$

Where Brillouin function

$$B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{x}{2J}.$$

For small values of x it is approximately linear

$$B_J(x) = \frac{J+1}{3J} x + \mathcal{O}(x^3).$$

For large x, it approaches 1 for all J. As the field gets strong, all dipoles align parallel to the field, so $\mu = g\mu_B J$ For large spin we have

$$B_J(x)\big|_{J \gg 1} = L(x) = \coth x - \frac{1}{x},$$

This is the Langevin function, it is the classical limit of magnetization. In the other limit, the minimum is $J = 1/2$ and the Brillouin function simplifies to

$$B_{\frac{1}{2}}(x) = 2\coth 2x - \coth x = \frac{1 + \coth^2 x}{\coth x} = \tanh x.$$

With the exception of very small temperatures, we can use the linear approximation, this gives

$$M = Nm = \frac{Ng^2\mu_B^2 J(J+1)B}{3kT}.$$

And the susceptiblity

$$\chi = \frac{Ng^2\mu_b^2 J(J+1)B}{3kT}.$$

This is sometimes referred to as Curie's law, where

$$M = C\frac{B}{T}, \qquad \chi = \frac{C}{T}.$$

Ferromagnetic materials

For high temperatures (much higher than the curie temperature T_C), a ferromagnetic material behaves as a paramagnetic one, as described by the Curie-Weiss law

$$\chi = \frac{C}{T - T_C}.$$

The big difference is there is a phase change at $T = T_C$ where the susceptibility diverges, at temperatures below the Curie temperature, the material spontaneously magnetize. Experiment shows that the susceptibility diverges like

$$\chi \propto |T - T_C|^{-\gamma}.$$

Where $\gamma = 1.4$. We also find that

$$C_B \propto |T - T_C|^{-\alpha}.$$

Interacting dipoles

However, in real materials, the orientation of a specific dipole will depend and affect the orientation of at least it's closest neighbors. A material where the magnetic dipoles tend to be oriented in the same direction is a *ferromagnet*, this will lead to magnetic domains and the material can have a spontaneous magnetization even when there is no external magnetic field. A material where the dipoles tend to be oriented in the opposite direction of their neighbors is called a *antiferromagnet*.

A ferromagnet will have spontaneous magnetization at low temperatures, as the temperature increases, the magnetization reduces slowly. At the curie temperature there is a phase change and any total magnetization vanishes.

Ising model

We neglect any long range interaction between dipoles, and let only dipoles affect the closest dipoles. We focus on a single domain in a ferromagnet. (Note that the ising model is a very simple model, at low temperature the model fails, as it should describe the long-wavelength *magnons*), however, at temperatures close to the Curie temperature, this simple model is remarkably good.

We say that a neighboring pair of dipoles carry an energy ϵ if they are aligned the same way, and $-\epsilon$ if they are aligned oppositely. So we have

$$U = -\epsilon \sum_{\text{neighboring pairs}} s_i s_j.$$

Calculating the partition function in 2D is very difficult as the number of system structures grows as 2^N.

Exact solution in 1D

In 1D, each dipole only has two neighbors, so we can find the partition function exactly

$$U = -\epsilon \sum_{i=1}^{N-1} s_i s_{i+1} = -\epsilon(s_1 s_2 + s_2 s_3 + \ldots s_{N-1} s_N).$$

And so the partition function becomes

$$Z = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} e^{-\beta U(s_1, s_2, \ldots, s_N)} = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} e^{\beta \epsilon s_1 s_2} e^{\beta \epsilon s_2 s_3} \cdots e^{\beta \epsilon s_{N-1} s_N}.$$

Where every sum is over ± 1. Not that the last Boltzmann factor is the only one that depends on s_N, so we can pull all the other factors out of the s_N sum, and we have

$$Z = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_{N-1}} e^{\beta \epsilon s_1 s_2} e^{\beta \epsilon s_2 s_3} \cdots e^{\beta \epsilon s_{N-2} s_{N-1}} \sum_{s_N} e^{\beta \epsilon s_{N-1} s_N}.$$

And the final sum becomes

$$\sum_{s_N} e^{\beta \epsilon s_{N-1} s_N} = e^{\beta \epsilon} + e^{-\beta \epsilon} = 2 \cosh \beta \epsilon.$$

We can now do the same for the s_{N-1} sum, and get the same result. We do this all the way down to the s_2 sum and end up with

$$Z = \sum_{s_1} \left(2 \cosh \beta \epsilon \right)^{N-1}.$$

The final sum only contributes a factor of 2, so we need to do an approximation

$$Z = 2^N (\cosh \beta \epsilon)^{N-1} \approx (2 \cosh \beta \epsilon)^N.$$

From this we get the energy

$$U = -\frac{\partial}{\partial \beta} \ln Z = -N \frac{\sinh \beta \epsilon}{\cosh \beta \epsilon} \epsilon = -N \epsilon \tanh \beta \epsilon.$$

Which goes to $-N\epsilon$ as $T \to 0$, i.e., all dipoles align as $T \to 0$ and $U \to 0$ as $T \to \infty$, i.e., all dipoles align randomly as high temperatures. (This is the same Z and U as for the paramagnet with $\epsilon = \mu B$, the difference is that the paramagnet makes all dipoles align along an external field, while the ising crystel just makes the dipoles align along their neighbors).

The heat capacity then becomes

$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = \frac{Nk(\beta\epsilon)^2}{\cosh^2(\beta\epsilon)}.$$

The 1D exact solution has a smooth energy transistions and *does not* give a critical temperature, to get the phase transistion we have to turn to the 2D ising model first solved by Onsager.

Mean field theories

We now look at a single dipole with spin s_i, somewhere in the interior of the lattice. Let n bethe number of nearest neighbors, we then have

$$n = \begin{cases} 2 & \text{in 1D;} \\ 4 & \text{in 2D (square lattice);} \\ 6 & \text{in 3D (simple cubic lattice);} \\ 8 & \text{in 3D (body-centered cubic lattice);} \\ 12 & \text{in 3D (face-centered cubic lattice).} \end{cases}$$

We now assume that the neighbors have frozen spins, and so our only degree of freedom is s_i. If we let j run over all the nearest neighbors of s_i we get

$$E_\uparrow = -\epsilon \sum_j s_j = -\epsilon\bar{s}, \qquad E_\downarrow = \epsilon\bar{s}.$$

And so the partition function for the isolated dipole becomes

$$Z_i = e^{\beta\epsilon n\bar{s}} + e^{-\beta\epsilon n\bar{s}} = 2\cosh\beta\epsilon n\bar{s}.$$

And from this partition function we can calculate the expectancy of s_i, getting

$$\langle s_i \rangle = \frac{1}{Z_i}\left[e^{\beta\epsilon n\bar{s}} - e^{-\beta\epsilon n\bar{s}}\right] = \frac{2\cosh\beta\epsilon n\bar{s}}{2\cosh\beta\epsilon n\bar{s}} = \tanh\beta\epsilon n\bar{s}.$$

Now the **fundamental approximation of the mean field approximation** is that we assume $\bar{s}_i = \bar{s}$. This means we assume the average magnetization is uniform across the entire lattice, and so all spins 'see' the same neighborhood. This gives the equation

$$\bar{s} = \tanh\beta\epsilon n\bar{s}.$$

And $\bar{s}$ now refers to the average magnetization dipole alignment across the entire lattice.

This equation is transcendental and cannot be solved on closed form. If we plot it out graphically, we see that we have to major cases. If $\beta\epsilon n < 1$, which

implies $kT > n\epsilon$, the slope of the hyperbolic tangent is so low that there is only one solution, at $\bar{s} = 0$, i.e., there is no net magnetization of the material. For $kT < n\epsilon$, there are three solutions, an unstable solution at $\bar{s} = 0$ and two stable ones, located symmetrically around the center. This means the system will acquire a net nonzero magnetization, which is equally likely to be positive or negative.

We see that the critical temperature is the temperature where $kT_c = n\epsilon$, since this is when we go from having a single to three solutions. The critical temperature is thus proportional to both the coupling strength and the number of neighbors, no shock there. Note that the mean field approximation predicts a critical temperature even in 1D, which we did not find in our analytical answer—this is simply because the simple mean field approximation is terrible in 1D.

Brownian Motion and the Langevin equation

Einstein Relation

A system of diffusive particles will be in equilibrium where there is a downward flux due to gravity, and an upward flux due to diffusion

$$\mu C(x,t)mg = -D\frac{\partial C}{\partial z}.$$

Where z is the vertical coordinate, mg is the gravitation on each particle, D is the diffusion constant and μ is the mobility, which is the velocity a particle moves through a fluid with when acted on with a force F, so $\mu = v/F$.

Now, due to equilbrium, the particles will follow a Boltzmann distribution along the height of the cylinder, as the potential field increases linearly upwards, so **at equilbrium**:

$$C(x,t) \propto e^{-\beta mgz}.$$

Which gives

$$\frac{1}{C}\frac{\partial C}{\partial z} = -\beta mg.$$

And so

$$D = \mu kT.$$

And this is the Einstein Relation. It links the mobility, a macroscopic observable that is independant of fluctuations, to a direct measurement of fluctuations. It is therefore referred to as the fluctuation-dissipation relation, since μ determines the viscous dissipation that occurs when a particle is moved.

Langevin equation

The langevin equation is Newton's 2. law for a Brownian particle. It is subject to viscous drag from the surrounding fluid, and also the impacts from local fluid molecules. Since there will be many random collisions affecting the particle, we can turn to the central limit theorem. If we let δp_i denote the x-component of the momentum transfer. We denote the number of collisions during a time Δt by N, so ΔP is the sum of all N contributions. The momentum change over time corresponds to a force, which will have variance

$$\langle F_x^2 \rangle = \frac{\langle \Delta P^2 \rangle}{\Delta t^2} \propto \frac{1}{\Delta t}.$$

And if we solve the Langevin equation numerically, we can draw the force as a normal number, as long as the time-step is long enough for the force contributions to be uncorrelated.

So we have $\langle \tilde{F} \rangle = 0$, and the viscous force is given by Stokes law, so we have

$$m\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = -\alpha\vec{v} + \tilde{\vec{F}}.$$

From the Langevin equation we can show that

$$\langle x^2 \rangle(t) = \frac{2kT}{\alpha}\left(t - \frac{m}{\alpha}(1 - e^{-\alpha t/m})\right).$$

On a short time scale, ineratial effects, $m\mathrm{d}^2 x/\mathrm{d}t^2$ are important, on long time-scales, they are ignored, and we simplify to a random walker.

$$\langle x^2 \rangle(t) = \begin{cases} \frac{kT}{m}t^2 & \text{for } t \ll m/\alpha, \\ \frac{kT}{m}t & \text{for } t \gg m/\alpha. \end{cases}$$

Ideal gas

An ideal gas consist of N particles, where each particle only carries an energy of
$$\epsilon = \frac{p_x^2 + p_y^2 + p_z^2}{2m}.$$

The Partition function must sum over all possible states
$$Z = \sum_s e^{-\beta E(s)},$$

so we must find some way to quantize momentum, putting the ideal gas in a box gives
$$k_i = \frac{n\pi}{L}.$$

And so we have $p_i = \hbar k_i = n\hbar\pi/L$, giving for one dimension:
$$Z_{1d} = \sum_n e^{-\beta E_n} = \sum_n \exp\left(-\frac{\beta\hbar^2\pi^2}{2mL^2}n^2\right).$$

For a macroscopic L and a T not to close to 0, there will be extremly many modes, and so we can approximate the sum by the corresponding integral, giving
$$Z_{1d} = \int_0^\infty \exp\left(-\frac{\beta\hbar^2\pi^2}{2mL^2}n^2\right)\,\mathrm{d}n = \frac{\sqrt{\pi}}{2}\sqrt{\frac{2mL^2}{\beta\hbar^2\pi^2}} = \sqrt{\frac{m}{2\pi\beta\hbar^2}}L = \frac{L}{l_Q}.$$

Where we have defined the quantum wave-length
$$l_Q \equiv \frac{2\pi\beta\hbar^2}{m}.$$

In three dimensions, we then find
$$Z_{3d} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta E(n_x+n_y+n_z)} = \sum_{n_x} e^{-\beta E n_x}\sum_{n_y} e^{-\beta E n_y}\sum_{n_z} e^{-\beta E n_z} = \frac{L}{l_Q}\frac{L}{l_Q}\frac{L}{l_Q} = \frac{V}{v_q}.$$

This is usually just written as
$$Z = \int \frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} e^{-\beta p^2/2m} = \frac{V}{v_q}.$$

using semi-classical arguments.

And so
$$Z_n = \frac{1}{N!}\left(\frac{V}{v_q}\right)^N.$$

Van der Waals equation

Reactions

The chemical potentials at equilibrium follow the exact same formula as the reaction equation itself. Consider for example the creation and annihilation of electron-positron pairs

$$e^+ + e^- \Leftrightarrow \gamma.$$

We then immediately have

$$\mu_{e^+} + \mu_{e^-} = \mu_\gamma.$$

And since we can reasonably assume that $\mu_{e^+} = \mu_{e^-}$ we get that they are both zero.

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Vanlig Z, U, C_V osv for

- Harmonisk oscillator (Einstein Solid)
- Paramagnet
- Ideel gass
- Fermiongass
- Photongass